An introduction to thermodynamics

Basic algorithm of thermodynamics

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Everything about ES 181 2019.

This book aims to help you master thermodynamics. I will keep updating the book, and draw figures in class. Please access the current version of this book online, and keep notes in class.

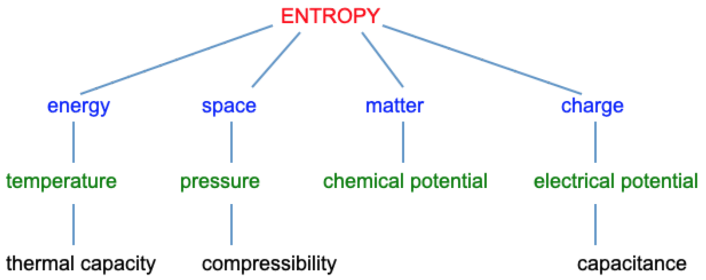
The play of thermodynamics

In class, I do not cover this section in one go. I pick a bit at a time, throughout the semester. I do start the course by introducing the cast of the play.

The cast

Leading role. Thermodynamics is often called the science of *energy*. This designation steals accomplishments from other sciences, and diminishes accomplishments of thermodynamics. Rather, thermodynamics is the science of *entropy*. Entropy plays the leading role in thermodynamics.

Energy crisis is a timely topic; entropy crisis, timeless.



Supporting roles. In thermodynamics, energy plays a supporting role, along with space, matter, and charge. These supporting roles are analogous, of equal importance.

Calling thermodynamics the science of energy confuses the structure of the play. Energy, space, matter, and charge obey a similar law—*the law of conservation*. Entropy alone obeys a different law—the *law of generation*. Of all laws of Nature, entropy alone gives an inequality. Nature singles entropy out. So should our play.

Children and grandchildren. Each of the supporting roles, together with entropy, produces a child. The four children—temperature, pressure, chemical potential, and electrical potential—are the second generation of supporting roles. They produce grandchildren: thermal capacity, compressibility, coefficient of thermal expansion, Joule-Thomson coefficient, etc.

Shadows of entropy. Entropy casts many shadows: Massieu function, Planck function, Helmholtz function, Gibbs function, exergy, etc. Let no shadows divert our attention from the real thing—entropy.

The Cast of Thermodynamics

Leading role:
Entropy

Supporting roles:
Energy
Space
Matter
Charge

Children of entropy and the supporting roles:
Temperature
Pressure
Chemical potential
Voltage

Grandchildren:
Thermal capacity
Compressibility
Coefficient of thermal expansion
Joule-Thomson coefficient
…...

Shadows of entropy:
Massieu function
Planck function
Helmholtz function
Gibbs function
Exergy
…...

Thermodynamics for everyone

Thermodynamics should be a play for everyone, just as English, physics, chemistry, and calculus should. The logic of thermodynamics is expressed mostly in English, with a little physics, chemistry, and calculus. I'll be careful in using English, and even more careful in using physics, chemistry, and calculus.

English is a wonderful language, but is not invented for thermodynamics. The facts of physics, chemistry, and calculus are not hard, but applying them can be challenging. I will mostly use nouns and verbs, and mostly avoid adjectives. Along with words, I will use pictures, videos, and equations. A picture is worth a thousand words. A video is worth a thousand pictures. An equation is worth a thousand videos. You experience thermodynamics in daily life and you will do experiments in labs.

A girl meets a boy. They fall in love. They live happily ever after. How many times have we heard this story? Yet we keep telling this story. Each telling is as fresh as that by Homer or Shakespeare. It is a great story, has endless variations, and is fundamental to many other stories. It is a story to experience for a lifetime.

So is thermodynamics. This book is my version of the story of thermodynamics. And this version is just one of my many versions! I have published many research papers in which thermodynamics plays out in various ways.

After this course, you will recognize the story of thermodynamics no matter who tells it. Aha, you will say, this is yet another play of thermodynamics! One day, you will tell your own story of thermodynamics. You cannot avoid telling the story so long as you stay in touch with Nature. Thermodynamics is a fundamental play of Nature.

History

This book does not teach the history of thermodynamics. It is impractical to teach thermodynamics by tracing the steps (and missteps) of Carnot, Clausius, Boltzmann, and Gibbs, just as it is impractical to teach calculus by tracing the steps of Newton and Leibniz. A subject and its history are two different things. Mixing them in an introductory book does injustice to both.

This said, the history of thermodynamics is interesting, illuminating, and well-documented, full of dramas of triumph and despair. Nature works without science. It is humans who create science to understand Nature. To study science is to study Nature *and* humans. We celebrate past creators, and nurture future ones. We build a collective memory that helps humans survive, prosper, and find happiness.

Missteps of the creators leave scars on thermodynamics, some of which are unhealed to this day. Healing may expedite if we learn some history.

I will place a few names and years in this book as landmarks. You can read the history of thermodynamics online, starting with this Wikipedia entry.

But historians do not create history. You might as well dip into original works, many of which are available online in English. Even a cursory reading of the works by the creators will enhance your enjoyment of the play. Stars shine before street lamps pollute the sky.

Logic, intuition, and application are distinct aspects of thermodynamics

Open a text of physics, chemistry, biology, environmental science, or materials science, and you see large sections on thermodynamics. Entropy affects all macroscopic phenomena.

The ubiquity comes because entropy is the universal force of Nature, but the ubiquity also makes entropy difficult to learn. To apply entropy to an engine, for example, you need to know entropy *and* the engine. Mixing the logic of entropy and the operation of the engine confuses a beginner.

This book will develop the *logic* of entropy from first principles, *intuition* of entropy from everyday experience, and *application* of entropy in many domains.

I will keep the logic, intuition, and application in separate sections. In particular, I forgo the historical development, and do not use the operation of an engine to develop the logic of entropy. This historical development was hard in creating thermodynamics, and is even harder today. Students today rarely have first-hand knowledge of engines, and many may not even care about engines.

logic

The logic of thermodynamics requires five ideas: isolated system, sample space, property, state, and equilibrium.

- An *isolated system* is a part of the world that does not interact with the rest of the world.
- An isolated systems flips—rapidly and ceaselessly—to *a set of quantum states*. In the language of probability, the isolated system is called an *experiment*, each quantum state is called a *sample point*, and the set of all quantum states of the isolated system is called the *sample space*.
- An *internal variable* x is a function that maps the sample space to a set X, such as a set of values of energy, values of volumes, numbers of a species of molecules, and amounts of charge. An internal variable is called a *random variable* in probability, and is called a *property* in thermodynamics.
- When an internal variable is fixed at a value x in a set X, the isolated system flips among the quantum states in a *subset* of the sample space. Denote the number of quantum states in this subset by Ω(x). A subset of the sample space is called an *event* in probability, and is called a *state* in thermodynamics.
- After the system is isolated for a long time, and after an internal variable is fixed at a value x for a long time, the system flips to every quantum states in the subset with equal probability. The isolated system is said to reach *equilibrium*.

The logic of thermodynamics parallels that of probability. We will only need a few basic ideas of probability. A course on probability is not a prerequisite for learning thermodynamics.

When the internal variable is fixed at a value x, define the *subset entropy* by S(x) = log Ω(x). Entropy is a dimensionless, absolute, extensive, thermodynamic property.

Intuition

To develop intuition, we will look at familiar phenomena:

- Ideal gas
- Ideal gas mixture. humidity, dew, frost
- Change of phases. Ice, water, steam
- Dispersion of ink
- Dissipation of energy
- Degradation of energy

I will remind you of empirical facts—things that you already know. I will stay focused on the logic of entropy, rather than overwhelm you with facts specific to individual phenomena. Multidisciplinary study is effective if we are disciplined.

Application

Thermodynamics makes ordinary ideas extraordinarily effective. The range of application is enormous, as rich as Nature itself. Any one of the standard textbooks will have copious examples. This book will describe some:

- Pure substance
- Incompressible pure substance
- Ideal gas
- Ideal gas mixture
- van der Waals model
- Osmosis
- Steady-flow devices (e.g., turbine, compressor, throttle, heat exchanger, nozzle, and diffuser)
- Cycles
- Power plants
- Refrigerators
- Internal combustion engines
- Heating, ventilation, and air-conditioning
- The ascent of sap
- Chemical reactions

- Fuel cell

All these applications, particularly engines, historically contributed to the development of thermodynamics. But all applications are incidental to the logic of thermodynamics. You can master thermodynamics without studying engines.

The situation is similar in calculus. The calculation of the orbits of planets historically contributed to the development of calculus, but is incidental to the logic of calculus. You can master calculus without studying the orbits of planets.

Basic algorithm of thermodynamics (BAT)

Every thermodynamic phenomenon, reduced to its core, can be analyzed using the basic algorithm of thermodynamics (BAT), in four steps:

- Construct an isolated system with an *internal variable* x.
- Find the *subset entropy* of the isolated system as a function of the internal variable, S(x).
- Keep the subset entropy constant for a *reversible process*, including *equilibrium*.
- Increase the subset entropy for an *irreversible process*.

When a phenomenon requires an isolated system with multiple internal variables, each being a function from the sample space to a distinct set, the BAT runs just the same. This course will run the BAT on many phenomena.

Ignore the laws

I will not structure this play of thermodynamics around the zeroth, first, and second laws. It is often claimed that these laws define the three thermodynamic properties: temperature, internal energy, and entropy. This claim is false, and confuses even experienced scholars. No one practices thermodynamics with these laws. They are sterile.

The situation is reminiscent of Chinese medicine. The medicine works, but the theory of medicine is faulty, made up before the facts of Nature came to light.

I will mention the laws of thermodynamics in passing, so you see how they mislead. I will focus on the basic algorithm of thermodynamics that directs calculation and experiment, in a way that thermodynamics has been practiced since the time of Gibbs (1873).

Postulates and facts

I play down the “laws of thermodynamics” for another reason. The Euclidean geometry must have made a deep impression on the creators of thermodynamics. In Euclidean geometry, a few facts, labeled as postulates (i.e., laws), derive all other facts.

Thermodynamics has never been practiced this way. A few facts do play special roles in setting up the basic algorithm, but are insufficient to derive most other facts. For example, we will use the basic algorithm to develop a theory of temperature and a theory of melting, but these theories do not predict this fact: ice melts at zero Celsius.

Euclidean geometry is a wrong model for thermodynamics, and is even a wrong model for practical use of geometry. In thermodynamics, numerous facts are significant, and cannot be derived from other facts. You will have to learn numerous facts individually.

Watch the Feynman Lecture on the relation between mathematics and physics. (The discussion on Greek and Babylonian traditions of mathematics starts at 23:30.)

Big data

Nature generates big data of thermodynamics. The BAT guides us to measure, curate, and use the big data.

Thermodynamic data are measured in many ways, including thermometry, calorimetry, thermochemistry, and electrochemistry.

Steam tables list temperature, pressure, volume, energy, enthalpy, and entropy of a single species of molecules, H_2O, in various states. Similar tables exist for numerous other pure substances, most notably for refrigerants.

For each species of molecules, ideal gas tables list enthalpy and entropy as functions of temperature. These tables are used to analyze mixing and reaction of any number of ideal gases.

Solids and liquids that mix many species of molecules generate enormous amounts of data. Their gathering remains an unfinished business, and has become a part of the Material Genome Initiative.

Concrete examples

A logical place to start the book is the basic algorithm of thermodynamics. However, this logical starting point is removed from everyday experience.

Thermodynamics is an abstract subject, but has numerous concrete examples. We will begin with four:

- ideal gas
- relative humidity

- incompressible pure substance
- pure substance.

I will divide the last example into two sections, one devoted to water and steam, and the other to ice, water, and steam. These examples motivate the logic of thermodynamics, sharpen our intuition, and underlie numerous applications. We will return to these examples throughout the book.

Ideal gas

A collection of molecules is called an *ideal gas* if the individual molecules are far apart on average. That is, the distance between two molecules on average is much larger than the size of an individual molecule. The molecules move rapidly and ceaselessly. They fly, collide, and separate.

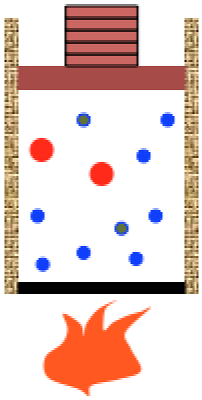
Fact. To a good approximation, air is an ideal gas. Air consists of mainly nitrogen and oxygen molecules, along with small fractions of other molecules. Wiki atmosphere of Earth.

Fact. The discovery of molecules dates back thousands of years, from hypothesis to confirmation. We are all made of molecules. So are plants, animals, rivers, and mountains. Wiki molecule.

For example, H_2O is a molecule of two hydrogen atoms and one oxygen atom. The expression H_2O is called the *chemical formula* of the molecule, indicating both the species of atoms in the molecule and the number of atoms in each species.

An experimental setup

An experimental setup consists of a gas, cylinder, piston, weight, and fire. The setup lets us measure four quantities: N, V, P, T.



Number of molecules N. We seal a cylinder with a piston. The piston can move up and down, but molecules cannot leak in or out. The cylinder holds a fixed number of molecules, N.

Assume that all molecules in the cylinder are of the same species, such as nitrogen N_2. Let M be the mass per nitrogen molecule. We can weigh the mass of the gas in the cylinder, m. The number of molecules in the cylinder is

$N = m/M$.

If the molecules in the cylinder belong to several species, “counting” the number of molecules becomes more cumbersome. We will describe methods later.

Volume V. The volume of the cylinder, V, equals the base area of the cylinder, A, times the height of the piston, z:

$V = Az$.

When the piston slides up and down, the cylinder changes volume.

Pressure P. To measure the pressure of the gas in the cylinder, P, we place blocks of mass on top of the piston. By a *weight above the piston* we mean the force acting on the piston due to blocks of mass and the pressure of the surrounding air:

weight = $mg + P_{air}A$.

Here m is mass, g is the acceleration of gravity, P_{air} is the pressure of surrounding air, and A is the base area of the cylinder. The mass m also includes mass of the piston.

Assume that the piston slides against the cylinder with no friction. The balance of the forces acting on the piston relates the force of the weight to the pressure of the gas in the cylinder: weight = PA. Thus,

$P = P_{air} + mg/A$.

By changing the mass of the blocks placed over the piston, we change the pressure of the gas in the cylinder.

Exercise. The pressure of the air is measured using a *barometer*. Wiki barometer. How does a mercury barometer work? Why is mercury used, not water?

Exercise. Estimate the total mass of the atmosphere of the Earth. The atmospheric pressure is about 100 kPa. The radius of the Earth is about 6400 km.

Exercise. What is the pressure at 10 m beneath the surface of an ocean?

Temperature T. We change the temperature of the gas, T, by placing the cylinder over a fire.

How do we measure temperature? Use a thermometer, of course. But what is a thermometer? It is an instrument to measure temperature. What is temperature? It is a quantity measured by a thermometer. Such circular questions and answers are useful in kindergartens. They relate temperature and thermometer, but explain neither.

Fact. Galileo (1610s) and his contemporaries invented the first thermometer using a bulb of air! For a fixed amount of air and a fixed pressure, as the air heats up, it expands in volume. Thus, the volume is a proxy for the temperature.

Exercise. YouTube Galileo's gas thermometer. Explain how it works.

Ideal gas law

What is temperature? I have mentioned the modern answer: temperature is the child of the union of entropy and energy. This answer will become precise after we know the parents—entropy and energy.

But the relation between temperature, energy, and entropy was discovered in the 1850s, and was unknown to Galileo and his contemporaries. They defined temperature using an empirical fact.

Fact. Two bulbs of air are prepared, each having its own values of N, V, P, T. Bring the two bulbs in contact, called *thermal contact*. In thermal contact, each bulb keeps its amount of air, but changes its volume, pressure, and temperature.

The two bulbs are said to have the same temperature—and in *thermal equilibrium*—when the volumes and pressures stop changing.

Ideal gas temperature. Experiments like this, in the course of centuries, led to a discovery. In thermal contact, two bulbs of ideal gases stop changing volumes and pressures when the values of PV/N of the two bulbs equalize.

This experimental discovery prompted a brilliant idea: PV/N of an ideal gas defines temperature T. This idea is stated as the *ideal gas law*:

$$PV = NT.$$

The temperature so defined is called the *ideal gas temperature*. The product PV has the unit of energy, Joule, and N is dimensionless. Consequently, the ideal-gas temperature T has the same unit as energy, Joule.

Fact. As we will see later, the ideal gas temperature coincides with the modern definition of temperature.

Aside: history of the ideal gas law.

Inconvenient units. The ideal gas law in the above form is inconvenient for everyday use for two reasons. First, the number of molecules, N, in a bulb is an extremely large number. Second, the temperature in the unit of energy is an extremely small number.

Boltzmann constant

Kelvin. To fix the second problem, people report temperature using another unit, Kelvin. The 2019 redefinition of the SI base units defines the conversion of the two units—Kelvin and Joule—by

1 Kelvin = 1.380649×10^{-23} Joules.

The conversion factor is called the Boltzmann constant k_B. For practical calculation, take

$k_B = 1.38 \times 10^{-23}$ J/K.

Caution. It is comical to attach an unsightly number to three giants: Boltzmann, Joule, and Kelvin. If this number intrigues you, wiki Boltzmann constant. If not, you miss nothing.

Any conversion of unit is as mundane as 1 inch = 2.54 centimeters. In honor of two teaching fellows, I propose that we name centimeter by Ding and inch by Kim. In honor of our head teaching fellow, I propose that we name the Steck constant: j_S = 2.54 Ding/Kim.

Modern Celsius. The modern Celsius C is defined by

C = T − 273.15 K (T in the unit of kelvin).

The modern Celsius differs from the historical Celsius. The melting point and the boiling point of water are no longer used to define the modern Celsius. Rather, these two temperatures are determined by experimental measurements. The experimental values are as follows: water melts at 0°C and boils at 99.975°C.

The merit of using Celsius in everyday life is evident. It feels more pleasant to hear that today's temperature is 20 Celsius than 293.15 Kelvin, or 404.74×10^{-23}Joule.

Exercise. Confirm that 20 Celsius = 293.15 Kelvin = 404.74 × 10^{-23}Joule.

Exercise. Queen Snob defines a unit of temperature in which the melting point of gold is set to be 0 Snob, and the boiling point of gold is set to be 100 Snob. Derive the formula that converts Snob to Celsius.

Exercise. How was Celsius originally defined? What made the international committee redefine it?

Exercise. How would the international committee justify the definition of the conversion factor 1.380649 × 10^{-23} Joule = 1 Kelvin? Wiki Boltzmann constant.

k_BT is temperature in the unit of energy. When T is in the unit of Kelvin, $k_B T$ is temperature in the unit of energy, and the ideal gas law becomes that

$PV = Nk_BT$.

Nature's unit vs. human's unit. The Boltzmann constant k_B has no significance in Nature; it merely converts two units of temperature, Joule and Kelvin. The unit of energy is Nature's unit of temperature. Kelvin is a human's unit of temperature. Nature is indifferent to how humans define a unit for temperature. For any result of Nature, if T is in the unit of Kelvin, the product $k_B T$ must appear together. Thus, the introduction of the unit Kelvin clutters all results of Nature with the factor of conversion between the two units of temperature, the Boltzmann constant k_B.

Incidentally, many people call $k_B T$ thermal energy. This designation is in general incorrect. There is no need to give any other interpretation: when T is the temperature in the unit of Kelvin, $k_B T$ is simply the temperature in the unit of energy.

Avogadro constant

Mole. The number of molecules in a bulb, N, is enormous, and is inconvenient to report. To remove this inconvenience, a unit of amount is introduced, called *mole*. The 2019 redefinition of the SI base units defines a mole as

1 mole = 6.02214076 × 10^{23} items.

This conversion factor is called the Avogadro constant N_A. Wiki Avogadro constant if you are curious about the origin of Avogadro constant. For practical calculation, take

N_A = 6.022 × 10^{23} items/mol.

Nature's unit vs. human's unit. The Avogadro constant N_A has no significance in Nature; it merely defines a unit of amount, mole. A single water molecule is the Nature's unit for the amount of water. A mole of water is a human's unit for the amount of water. For any result of Nature, if the amount of items, n, is in the unit of mole, the product nN_A must appear together. Thus, the introduction of the unit mole clutters all results of Nature with the factor of conversion between the two units of amount of items, the Avogadro constant N_A.

Exercise. The ideal gas law can also be used to deduce the number of molecules in a gas. Through measurement we have found air at 25 Celsius and 100 kPa. We may approximate 1 mole of air as a mixture of 0.21 mole of oxygen and 0.79 mole of nitrogen. Calculate the number of nitrogen molecules and the number of oxygen molecules in 1 m^3 of air.

Exercise. How would you defend the choice of the conversion factor, $6.02214076 \times 10^{23}$ items = 1 mole of items? Wiki Avogadro constant.

Gas constants, universal and specific

Universal gas constant. If we use mole as a unit for the amount of gas, n, and use Kelvin as a unit for temperature, T, the ideal gas law becomes that

$PV = nRT$,

where

$R = N_A k_B = 8.314\ JK^{-1}mol^{-1}$.

The quantity R is called the *universal gas constant*.

Caution.The phrase "the universal gas constant" sounds pretentious and misleading to the modern ear. The constant R is the product of two factors of unit conversion: Kelvin as a unit for temperature, and mole as a unit for amount of items. Neither unit has any fundamental significance. Furthermore, the constant R is not limited to gas, but appears whenever the units of temperature and amount are changed.

Molar mass. The mass of one mole of a substance is called the *molar mass* of the substance. The molar mass is approximately 18 g/mole for water, 12 g/mole for carbon, 32 g/mole for oxygen molecules, and 28 g/mole for nitrogen molecules.

Specific gas constant. Let the molar mass of a substance be M, the mass of the substance be m. The amount of substance in the unit of mole is n = m/M. The ideal gas law becomes that

$PV = m(R/M)T$.

The ratio R/M is called the *specific gas constant*, and is denoted by R by some authors. You need to look at the unit to see if the symbol R stands for the universal or specific gas constant. For H_2O, recall that the molar mass is M_{H2O} = 18 g/mol, so that the specific gas constant is

R/M_{H2O} = (8.314 J/K-mol)/(18 g/mol) = 0.46 kJ/kg-K.

Exercise. Calculate the mass density, specific volume, volume per molecule, and volume per mole of water molecules at a temperature of 200°C and a pressure of 100 kPa.

Exercise. How does the density of oxygen change with the elevation? Assume that temperature is constant.

Relative humidity

Air

Air is a mixture of oxygen and nitrogen molecules, with small fractions of other molecules. Wiki atmosphere of Earth.

In practical calculations, we often approximate 1 mole of air as a mixture of 0.21 mole of oxygen and 0.79 mole of nitrogen. The mass of a mole of oxygen molecules is 32 g. The mass of a mole of nitrogen molecules is 28 g. Consequently, the mass of a mole of air is

M_{air} = (0.21)(32 g) + (0.79)(28 g) = 28.8 g.

For air, the specific gas constant is

R/M_{air} = (8.314 J/K-mol)/(28.8 g/mol) = 0.289 kJ/kg-K.

Partial vapor pressure

Fact. The ideal gas law, $PV = Nk_BT$, is applicable to any mixture of molecules of different species, where N is the total number of molecules in the mixture.

Let V be the volume of a bottle of air, which consists of several species of molecules. Let N_{H2O} be the number of H_2O molecules in the bottle. The *partial vapor pressure* of H_2O in the bottle, P_{H2O}, is defined by

$P_{H2O}V = N_{H2O}k_BT$.

Exercise. Calculate the partial pressure of carbon dioxide in the air. On average, each mole of the air has 365×10^{-6} mole of carbon dioxide. The total pressure of the air is about 100 kPa.

Saturated vapor pressure

When a half bottle of water is capped for some time, inside the bottle, the H_2O molecules in the gas equilibrates with the H_2O molecules in the liquid. The gas in the capped bottle is said to be *saturated* with H_2O molecules, and the partial pressure of H_2O in the saturated gas is called the *saturated vapor pressure*.

Fact. The saturated vapor pressure is a function of temperature, $P_g(T)$. The saturated vapor pressure is approximately 3 kPa at room temperature, and approximately 100 kPa at 100 Celsius. For a more extensive list of the function $P_g(T)$, see a NIST PDF file.

T, C	P, kPa
-22	0.085
-20	0.104
-18	0.125
-16	0.151
-14	0.181
-12	0.218
-10	0.260
-8	0.310
-6	0.369
-4	0.438
-2	0.518
0	0.611
1	0.657
2	0.706
3	0.758
4	0.813
5	0.872
6	0.935
7	1.002
8	1.073
9	1.148
10	1.228
11	1.313
12	1.402
13	1.498
14	1.599
15	1.705
16	1.818
17	1.938

18	2.064
19	2.198
20	2.339
21	2.488
22	2.645
23	2.811
24	2.985
25	3.170
100	101.4

Evaporation and condensation. When the partial pressure of H_2O molecules in a gas near water is below the saturated vapor pressure, $P_{H2O} < P_g$, water will evaporate. When the partial pressure of H_2O in the gas is above the saturated vapor pressure, $P_{H2O} > P_g$, the H_2O molecules in the gas will condense into water.

Sublimation and condensation. When the partial pressure of H_2O molecules in a gas near ice is below the saturated vapor pressure, $P_{H2O} < P_g$, ice will sublimate. When the partial pressure of H_2O in the gas is above the saturated vapor pressure, $P_{H2O} > P_g$, the H_2O molecules in the gas will condense into ice.

Exercise. In normal cooking, the pressure inside the cooker is at atmospheric pressure (100 k Pa), so that the temperature inside the cooker is limited to the boiling point of water, 100 Celsius. In high pressure cooking, the pressure inside the cooker is above atmospheric pressure, so that the boiling point goes above 100 Celsius. Suppose the pressure cooker allows boiling at 120 Celsius, what is the pressure inside the cooker?

Relative humidity

At a given temperature T, in the absence of water and ice, in equilibrium, the partial pressure of water P_{H2O} is below the saturated vapor pressure $P_g(T)$. Define the *relative humidity* by

$$RH = P_{H2O}/P_g(T).$$

Wiki relative humidity.

A bottle of air

Here is an empty bottle. I uncap, fill the bottle with the air in the classroom, and cap. How many H_2O molecules are in the bottle?

Recall the definition of the partial pressure of H_2O in the bottle:

$$P_{H2O}V = N_{H2O}k_BT.$$

Let us use this equation to calculate N_{H2O}. We get the values for all other quantities in this equation as follows.

- The Boltzmann constant is $k_B = 1.38 \times 10^{-23}$ J/K.
- The students in the class agree that the temperature in the classroom is about 20 Celsius, so that T = 293.15 K.
- A student reads the label on the bottle, and reports that the volume of the bottle is 500 ml. Thus, $V = 0.5 \times 10^{-3}$ m^3.
- How do we get the partial pressure of H_2O in the bottle? The value must be the same as that in the air of the classroom, because I have just filled the bottle with the air in the classroom. Recall the definition of the relative humidity: $RH = P_{H2O}/P_g$. A student in the class checks on the phone the weather report online, and finds that the relative humidity is 50%. The saturated vapor pressure at 20 Celsius is 2.3 kPa, according to the steam table. Thus, the partial pressure of H_2O in the bottle is 1.15 kPa.

These data give that

$$N_{H2O} = P_{H2O}V/(kT) = (1.15 \times 10^3 \text{ Pa})(0.5 \times 10^{-3} \text{ m}^3)/[(1.38 \times 10^{-23} \text{ J/K})(293.15 \text{ K})] = 1.4 \times 10^{20}.$$

The bottle contains enough H_2O molecules to give one H_2O molecule to every human that has ever lived, and more.

Note how we gather data from various sources.

Exercise. Estimate the number of H_2O molecules in the vapor in the half bottle of water that I used in class.

Dew point

At sunset, the temperature is 20 Celsius and the relative humidity is 50%. During the night, how much must the temperature drop for fog to form? The temperature to form fog is called the dew point. Dew point is also included in the weather report online. But let us estimate the dew point ourselves.

According to the table of saturated water, the saturated vapor pressure at 20 Celsius is P_g = 2.34 kPa. At relative humidity of 50%, the partial pressure of water is P_{H2O} = 1.17 kPa.

Look at the table of saturated water again. At a partial pressure of 1.17 kPa, water molecules in the air condense at about 9 Celsius. This temperature is the dew point.

The above estimate of the dew point assumes that the partial pressure of water keeps constant in the course of night before condensation. This assumption is wrong if the wind is strong, so that the composition of the air changes. Now let us assume that the air is still, and that the number of water molecules per unit volume in the air, N_{H2O}/V, is constant in the course of night before condensation. Recall the definition of the partial pressure, $P_{H2O}V = N_{H2O}kT$. When the temperature changes in the course of night, assuming constant N_{H2O}/V, the partial pressure of water in the air will change. But this change in partial pressure of water in the air will be small because the change in temperature is small: T changes from 293.15 K to 284.15 K in our example. Thus, to estimate the dew point in the still air, it is accurate enough to assume constant partial pressure of water in the air.

Exercise. At sunset, the temperature is 20 Celsius and the relative humidity is 30%. During the night, how much must the temperature drop for fog to form?

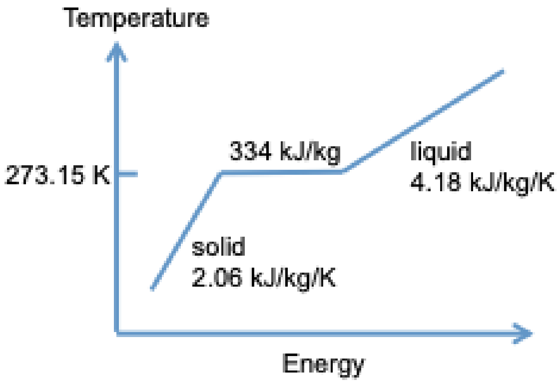
Exercise. Wiki frost. At sunset, the temperature is 5 Celsius and the relative humidity is 30%. During the night, how much must the temperature drop for frost to form?

Incompressible pure substance

Approximate water and ice as a thermal system

Steams can change volume greatly, but ice and water only change volume slightly. In considering ice and water, we often neglect the change in volume when H_2O molecules change state and phase. That is, in considering ice and water, we often approximate a fixed number of H_2O molecules as a thermal system.

This approximation represents the states of H_2O molecules as a single curve on the temperature-energy plane. We plot temperature T as the vertical axis, and the specific energy u as the horizontal axis. The function T(u) consists of three segments.



Energy of phase change

At the melting temperature, the function T(u) is a horizontal, straight segment. The left end of the segment represents the state of ice that begins to melt, and has specific energy u_s. The right end of the segment represents the state of water that begins to freeze, and has specific energy u_f. The difference in energy, $u_f - u_s$, defines the *energy of melting*, or the *energy of phase change*.

Rule of mixture

A point on the segment represents a mixture of ice and water. The H_2O molecules leave ice and become water: the temperature is fixed, but the energy changes. Let y be the mass fraction of ice in the mixture. The specific energy of the ice-water mixture is

$u = (1 - y)u_f + yu_s$.

This equation is the rule of two-phase mixture.

Thermal capacity

Below and above the melting temperature, the function T(u) is curved, but is commonly approximated by two straight segments with fixed slopes. One slope defines the *thermal capacity of ice*, and the other slope defines the *thermal capacity of water*.

The specific thermal capacity is 2.06 kJ/kg-K for ice, and 4.18 kJ/kg-K for water. The energy of phase change is 334 kJ/kg from ice to water.

Exercise. Calculate the energy needed to bring 1 kg of ice at -50 Celsius to liquid water at 50 Celsius.

Exercise. 1 kg of ice at the freezing temperature is mixed with 1 kg of water at the boiling temperature. The mixture is insulated. What will be the temperature in equilibrium?

Exercise. In 1845, James Joule presented experimental data to suggest that the water at the bottom of a waterfall should be warmer than at the top. His suggestion met great resistance from other scientists, partly because the change in temperature is small. For the Niagara Falls, about 50 m high, how much is the change in temperature?

Water and steam

A pure substance is a large number of a single species of molecules (or atoms). For example, a large number of H_2O molecules is a pure substance.

Phase

Here is a half bottle of water. One half of the bottle is filled with liquid, and the other half of the bottle is filled with gas. The half bottle of water is *not* half empty.

Fact. A species of molecules can aggregate into three forms: solid, liquid, and gas.

Each form is called a *(thermodynamic) phase*. For example, H_2O molecules form three phases: *ice*, *water*, and *steam*. YouTube ice, water, steam.

In a solid, molecules form a periodic lattice, called a *crystal*. Individual molecules vibrate near their sites in the lattice, and rarely jump out of the sites. Many small grains of the crystal form a bulk solid. Wiki ice.

In a liquid, molecules touch one another, but do not form a periodic lattice. Molecules change neighbors readily. They also rotate. Wiki water

In a gas, molecules on average are far apart. They fly, collide, and separate. Wiki steam.

A pure substance may form more than three phases. For example, H_2O molecules form multiple phases of ice at high pressure. Wiki ice. Each solid phase has a distinct crystalline lattice. This fact is neglected in this course, unless otherwise stated.

Incidentally, Percy Bridgman, who studied high-pressure phenomena at Harvard, won the 1946 Nobel Prize in Physics. He published extensively on thermodynamics.

Nobel lecture. Bridgman, General Survey of Certain Results in the Field of High-Pressure Physics, 1946.

Exercise. Write a few sentences on the usage of a few words: gas, vapor, fluid, steam, and air.

State

Fact. A pure substance isolated for a long time reaches equilibrium, called a *(thermodynamic) state*.

Phase and state are different concepts. A substance in a phase can change state. For example, steam—a phase—can be compressed to a smaller volume, or heated to a higher temperature. Steams in different volumes and different temperatures are different states, but all these states belong to the same phase—gas.

Fact. A pure substance can equilibrate in a single-phase state, a two-phase state, or a three-phase state.

For example, H_2O molecules can be in a single-phase state of ice, water, and steam. In a half bottle of water, the H_2O molecules equilibrate in a two-phase state, a mixture of water and steam. As we will see, H_2O molecules can also equilibrate in a three-phase state, a mixture of ice, water, and steam.

Fact. A pure substance cannot equilibrate in a state of four or more phases.

Property

A state-specific quantity is called a *(thermodynamic) property*.

Familiarity breeds contempt (and comfort). We will mostly talk about six properties: temperature, volume, pressure, energy, entropy, and enthalpy (TVpush). All six properties would look unfamiliar to antients.

When thermodynamics was created in the mid-nineteenth century, the creators were familiar with temperature, volume, and pressure, but had to invent energy, entropy, and enthalpy.

Most of you enter this course feeling comfortable with temperature, volume, and pressure, but not with energy, entropy and enthalpy. By the end of this course, you will be familiar with all six properties, and more. Familiarity breeds comfort. Civilization advances.

Fact. When a half bottle of water equilibrates, the water and steam have the same temperature. Such a property is called an *intensive property*. Pressure is also an intensive property.

Fact. When the half bottle of water equilibrates, the volume of the water and the volume of steam add to give the volume of the bottle. Such a property is called an *extensive property*. Mass is also an extensive property. So is the number of molecules. Later we will discuss other extensive properties, including energy, entropy, and enthalpy.

Specific volume

Both mass m and volume V are extensive properties. The ratio of mass over volume, m/V, defines the *mass density*. The ratio of volume over mass, V/m, defines the *specific volume*.

At room temperature and atmospheric pressure, the mass density of water is 1000 kg/m^3, and the specific volume of water is 0.001 m^3/kg.

We also report volume per molecule V/N, or volume per mole of molecules, V/n. Textbooks like to give V/m, V/N, and V/n distinct symbols. We will denote them all by v, and let the unit tell the difference. It is also common to use capital V to denote volume per molecule, per mole, or per unit mass. The context and unit will make it clear. No matter how careful we use words and symbols, only you can clarify an idea in your head.

Different books will use different symbols to denote the same quantity. A book may use one symbol to denote different quantities.

Being consistent is overrated. Train yourself to disregard symbols, and look for ideas. This said, let convention and common sense serve you. Using V to denote an area is unwise.

Exercise. At 25 Celsius, the partial pressure of H_2O molecules in steam is 3.170 kPa. A mole of water molecules has a mass of 18 g. Use the ideal gas law to estimate V/m, V/N, and V/n.

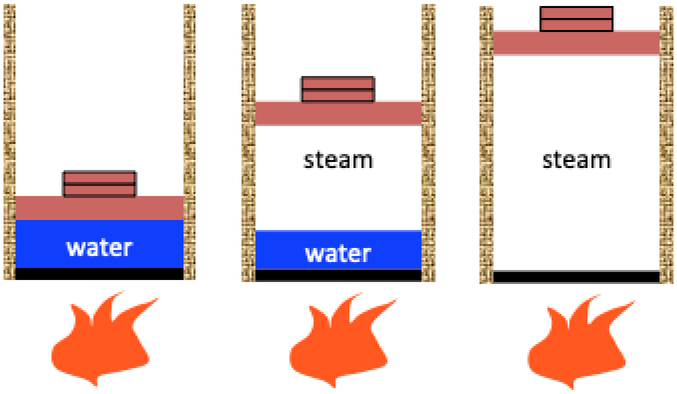
An experimental setup to study water and steam

Let us study water and steam using an experimental setup consisting of a cylinder, piston, weight, and fire.

Fix the number of H_2O molecules in the cylinder, N, by sealing the piston. Assume that the cylinder only contains H_2O molecules. As the piston slides up, the cylinder increases its volume, V. Vary the pressure inside the cylinder, P, by the weight above the piston. Vary the temperature inside the cylinder, T, by the fire under the cylinder.

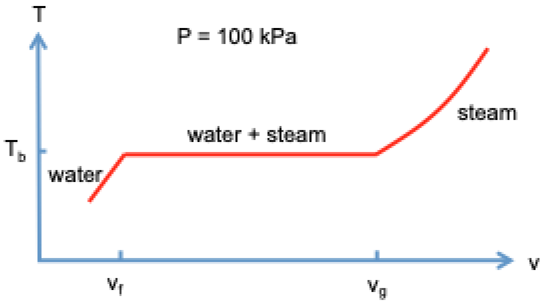
This experiment studies one pure substance (H_2O), two phases (water and steam), three properties (pressure P, temperature T, and volume V), and infinitely many states. (each state being specified by a value of temperature and a value of volume).

We do not need to study the effect of N. At fixed P and T, both V and N are proportional to the mass. We will report volume per unit mass, i.e., the specific volume v. The relation between N and mass is fixed: the molar mass of H_2O is 18 g/mol.



Temperature-volume plane

A pure substance has a few phases, which we name individually, such as solid, liquid, and gas. But we do not name individual states. A pure substance has infinitely many states, too many to name individually. Instead, we label each state by measurable quantities.



Fact. For a fixed amount of a pure substance, a state is specified by the values of two independent properties, such as volume and temperature.

The values of the two independent properties serve as an address—a name—of the state.

Consider a plane with volume and temperature as axes. Such a plane is called a *(thermodynamic) plane*. Volume is an extensive property, and temperature is an intensive property. Given an extensive property and an intensive property, it is a common practice to use the extensive property as the horizontal axis, and the intensive property as the vertical axis. Each point in the T-v plane represents a state of a unit mass of the pure substance.

Process

In the experimental setup, we now fix the pressure of the H_2O molecules in the cylinder by fixing the weight above the piston, and heat the H_2O molecules over the fire. We heat slowly, so that

H_2O molecules in the cylinder reaches equilibrium every time we collect a data point, a pair of values of T and v.

The temperature increases, the volume expands, and the H_2O molecules change state. A sequence of states is called a (*thermodynamic) process.*

When the pressure is fixed, the sequence of state is called a *constant-pressure process*. All states under a fixed pressure correspond to a curve in the T-v plane. Each point on the curve is a state of H_2O molecules. Let us follow a curve for a fixed pressure of 100 kPa. The curve has three segments.

Single-phase states of water. Below the boiling temperature, T_b, the H_2O molecules form water. As the temperature increases, the volume of the water expands.

Two-phase states of water-steam mixtures. At the boiling temperature, some of the H_2O molecules form water, and other H_2O molecules form steam. In coexistence, water and steam are said to be *saturated*. Upon receiving more energy from the fire, more molecules evaporates from water and join the steam: the mixture fixes the temperature at the boiling temperature, and expands volume.

Single-phase states of steam. Above the boiling temperature, all the H_2O molecules form steam. As the temperature increases, the volume of the steam expands.

When we remove the fire, the temperature-volume curve reverses, and the thermal energy inside the cylinder dissipates into the surroundings.

The liquid, gas, and liquid-gas are collectively called a *fluid*. A fluid flows because molecules in the fluid readily change neighbors.

Water expands on evaporation. In this example, the pressure is fixed at P = 100 kPa, and water boils at T_b = 99.62 Celsius (about 100 Celsius). At the boiling temperature, the specific volume of the saturated water is v_f = 0.001043 m^3/kg, and the specific volume of the saturated steam is v_g = 1.69400 m^3/kg. The subscript f stands for *flüssigkeit,* the German word for liquid.

Fact. The specific volumes of the two phases, water and steam, differ enormously. At 100 kPa, v_g/v_f is on the order of 10^3. Thus, in the saturated steam, molecules are, on average, at a distance of about the size of 10 molecules.

A fire causes the liquid to evaporate. The enormous expansion on evaporation converts fire to motion. This phenomenon is essential to steam engines and power plants.

Because of this enormous difference in specific volumes of water and steam, our sketch of the Tv diagram is unrealistic. To fit the diagram on a page, one can plot the specific volume in the logarithmic scale.

Exercise. In the liquid, molecules touch one another. Use the value of v_f to estimate the size of each H_2O molecule. What is the average distance between two H_2O molecules in the saturated steam at 100 C. How does the average distance between molecules compare with the size of a molecule?

Exercise. YouTube phase-change coffee mug. Explain the science of the phase-change coffee mug. What substance undergoes phase change? What are the phases? What characteristics of the phase change are significant to the coffee mug.

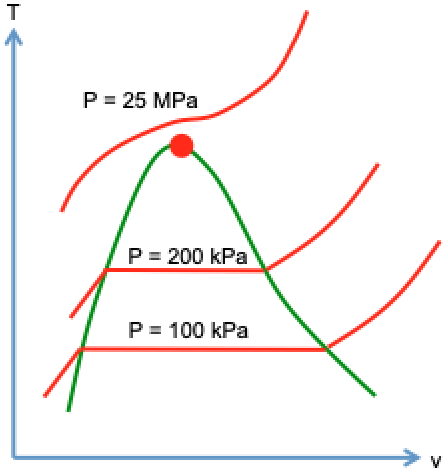
Liquid-gas dome

We can change the pressure by changing the weight above the piston. We now fix the pressure = at a new value, say P = 200 kPa. The state of H_2O molecules in the cylinder also changes as the fire heats the molecules. At this constant pressure, all the states of H_2O molecules fall on a curve in the temperature-volume plane. At P = 200 kPa, we find that

T_b = 120.21 Celsius
$v_f = 0.001060\ m^3/kg$,
$v_g = 0.88568\ m^3/kg$.

Fact. As the pressure increases, the difference in the specific volume of the saturated water and the specific volume of the saturated steam reduces. When the pressure is fixed at a value above a *critical pressure*, the difference in the two phrases disappears, and the states of H_2O molecules under a constant pressure fall on a smooth curve.

In the T-v plane, the region of water-steam mixture is inside a *dome*.



Critical state

The top of the liquid-gas dome is called the *critical state*, or *critical point*. The top of the dome is a thermodynamic state. For H_2O molecules, the critical state has the following properties:

T = 374.1 Celsius
P = 22.089 MPa
v = 0.003155 m^3/kg
u = 2029.58 kJ/kg
s = 4.4297 kJ/(kg-K)
h = 2099.26 kJ/kg

In addition to temperature T, pressure P, and specific volume v, we have listed specific energy u, specific entropy s, and specific enthalpy h.

Subject to a constant pressure above the critical pressure, a liquid state can change to a gaseous state without crossing the liquid-gas phase boundary.

Exercise. YouTube critical state. Mark the process observed in the experiment on the T-v plane. Does the experiment demonstrate the critical state?

Exercise. How would you demonstrate the existence of the critical state of a pure substance experimentally?

Rule of mixture

Inside the dome, each state—a pair of values of T and P—corresponds to a mixture of water and steam of some proportion. The volume of the mixture, V, is the sum of the volume of the water, V_f, and the volume of the steam, V_g:

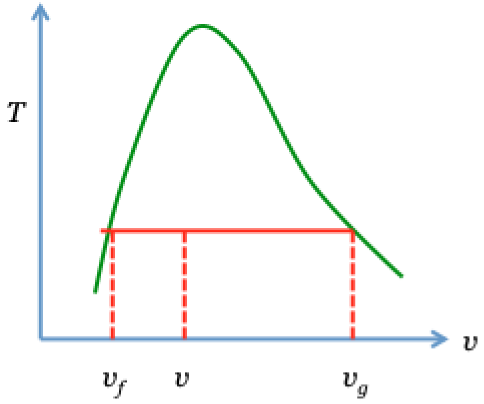
$V = V_f + V_g$.

The mass of the mixture, m, is the sum of the mass of the water, m_f, and the mass of the steam, m_g. The mass fraction of steam in the mixture, $x = m_g/(m_f + m_g)$, is called the *quality of the mixture*.

Define the specific volume of the water by $v_f = V_f/m_f$, the specific volume of the steam by $v_g = V_g/m_g$, and the specific volume of the mixture by $v = V/(m_f + m_g)$. Divide the equation $V = V_f + V_g$ by $m_f + m_g$, and these definitions lead to

$v = (1 - x)v_f + xv_g$.

This expression is called the *rule of mixture*, or the *lever rule*.



The rule of mixture applies to all extensive properties. For example,

$s = (1 - x)s_f + xs_g$.

The quality x itself is an intensive property. We can specify a state of water-steam mixture by a pair of values of P and x, for example.

Exercise. At 100 kPa, the specific volume of the saturated water is $v_f = 0.001043\ m^3/kg$, and the specific volume of the saturated steam is $v_g = 1.69400\ m^3/kg$. A tank of a volume of $1\ m^3$ contains a mass of 2 kg of H_2O. What is the mass of the steam in the tank?

Many functions of two independent variables

A pure substance has numerous properties. Seven examples are T, P, U, V, S, H, and x. We will introduce more properties, including thermal capacity, Helmholtz function, Gibbs function, compressibility, coefficient of thermal expansion, and Joule-Thomson coefficient.

A state of a pure substance is specified by values of two independent properties. Once a state is specified, every property takes a unique value. Thus, each property is a function of the two independent properties.

For example, for the seven properties, T, P, U, V, S, H, and x, a total of 24 pairs exist. Each pair can serve as independent properties, with caveats to be noted later. Thus, for each pure substance, a total of 120 functions of two variables exist. A great accomplishment of thermodynamics is to show that all these functions can be derived from a single function. We will describe this accomplishment in the coming lectures. For the time being, let us focus on the task of presenting many functions of two variables.

Exercise. There are more properties than the seven listed above. Let us add one more property to the list, the Helmholtz function F. For the eight properties, how many pairs exist? How many functions of two variables exist?

A function of two variables, f(x,y), can be presented in several ways.

Equation. Such an equation expresses a property as a function of two other properties, and is called an *equation of state*. An example is the ideal gas law, $kT = PV/N$. This method of presentation is practical for idealized models with simple equations of state.

Three-dimensional surface. A function f(x,y) is a surface in three dimensional space (x, y, f). This method is rarely useful in practice, because our common media of presentation—paper and screen—are two-dimensional.

Constant-property curves in a plane. In the x-y plane, plot curves of constant f. An example is the isotherms on the P-V plane.

Table. Given values of x and y, list the value of f. This method of presentation has prevailed for over two centuries, but has started to fade. For 120 functions, printed tables take many pages, and online tables are difficult to use. And these are just for one substance.

Calculator. The user inputs the values of two properties, the calculator outputs all other properties. Such calculators are available online and as apps.

Steam tables and steam apps

The thermodynamic properties of water and steam are presented using tables, called the *steam tables*. On-paper steam tables are fading out, just as on-paper maps are. Properties of steam and water live online and in apps.

Steam apps. Steam Tables Lite is a free iPhone app. To specify a state, the user enters the values of two properties, and the app displays the values of the other properties. The available pairs to be specified are PT, PH, PS, Px, Tx, HS.

Another iPhone app, Steam Pad, displays TS, HS, PH, and TH diagrams. The user can add and remove constant-property lines, and zoom in and out. The app also lets the user input any pair of properties in the list P, T, V, H, S, x. Why is U not in the list?

Yet another iPhone app, International Steam Tables, let the user enter values of PT, Px, PH, PS, HS, UV, HV. The app outputs the other properties. Also see the associated online property calculator.

Why does an app limit to few pairs of input? Why not let the user input any pair of properties? Does the memory of the phone place a list? The list of properties can be as long as that can fit on the screen of a phone. In coming years, steam apps will surely compete and excel.

Steam tables (old fashioned). We next describe the use of the NIST tables:

- NIST PDF (for water)
- NIST software (for many substances)
- YouTube steam table, Example 1, Example 2.

Inside the dome

The dome is formed by a smooth curve. The curve on the left is the specific volume of saturated water as a function of temperature, $v_f(T)$. The curve on the right is the specific volume of saturated steam as a function of temperature, $v_g(T)$.

For each pressure, the NIST table for saturation (pressure) lists the boiling temperature T, the specific volume of saturated water, v_f, and the specific volume of saturated steam, v_g. Also listed are specific entropies and enthalpies of the saturated water and saturated steam.

For example, at P = 100 kPa, the table lists the boiling temperature of 99.606 Celsius. The specific volumes and entropies of the saturated water and saturated steam are

$v_f = 0.001043\ m^3/kg$, $v_g = 1.6939\ m^3/kg$
$s_f = 1.3028$ kJ/kg-K, $s_g = 7.3588$ kJ-kg/K

Inside the dome, each point (T, v) corresponds to a state, a mixture of a state of saturated water and a state of saturated steam. In the mixture, the water and steam have the same temperature and the same pressure. A horizontal line through the point (T, v) intersects the curve of saturated water on the left and the curve of saturated steam on the right. The state (T,v) is a mixture of saturated water and saturated steam of some proportion.

Once a pressure is given, the table gives the boiling temperature. Thus, temperature is not an independent property. One more independent property is needed to specify a state. For example, a state can be specified by a pair of values P and v.

Given a value of P and a value of v, the quality x is determined by the rule of mixture $v = (1 - x)v_f + xv_g$, where v_f and v_g are found from the steam table for the given pressure.

Once x is determined, the entropy of the mixture is determined by $s = (1 - x)s_f + xs_g$, where s_f and s_g are found from the steam table for the given pressure. One can also determine the values of energy and enthalpy.

Exercise. 2 kg of H_2O has a pressure of 100 kP and a volume of 1 m^3. Use the NIST table (dome, pressure) to determine the energy and entropy.

Exercise. 1 kg of H_2O molecules has a temperature of 50 Celsius and a volume of 0.5 m^3. Use the NIST table (dome, temperature) to determine energy and entropy.

Exercise. On-paper steam tables use temperature and/or pressure as independent properties. This practice saves paper but wastes user's time. Of course, apps use no paper and aim to save user's time. Here is an illustration. 2 kg of H_2O has a volume of 1 m^3 and an energy of 4000 kJ. Determine the pressure. First try on-paper steam tables. Then try the app International Steam Tables, or the associated online property calculator.

Outside the dome

On a T-v plane, whereas a point inside the dome represents a *two-phase state*, a point outside dome represents a *single-phase state*.

Outside the dome, states of water and states of steam form a continuous region: no boundary divides states into liquid phase and gas phase. Some labels are used to name various parts of this region. Examples include compressed water, superheated steam, and supercritical fluid. Any labeling of a continuous region is arbitrary and should not distract us.

Outside the dome, the state can change continuously by independent change of temperature and pressure. Thus, temperature and pressure are independent properties. A pair of values (T,P) specifies a state outside the dome. Give a pair of values (T,P), the NIST table (outside the dome) lists volume, enthalpy, and entropy.

For example, at T = 400 C and P = 100 kPa, water molecules has the specific volume, specific enthalpy, and specific entropy:

v = 3.1027 m^3/kg
h = 3278.6 kJ/kg

s = 8.5452 kJ/kg-K

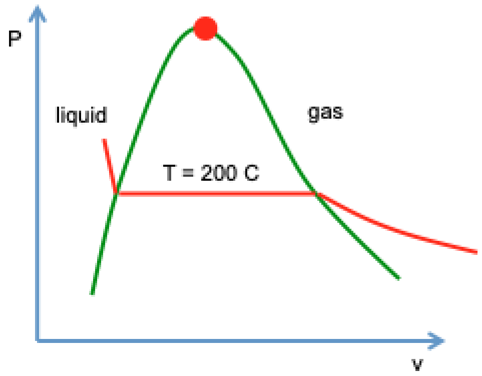
Exercise. Use the NIST steam tables to find specific volume, enthalpy, and entropy at the state of 200 C and 300 kPa.

Pressure-volume plane

Pressure is an intensive variable, and volume is an extensive variable. We use the specific volume v as the horizontal axis, and the pressure P as the vertical axis. Each point in the P-v plane corresponds to a state of a unit mass of a pure substance. Note a single-phase state of water, a single-phase state of steam, and a two-phase state of water-steam mixture.

All states of a fixed temperature correspond to a curve in the P-v plane, called an *isotherm*. This sequence of states of a constant temperature is called an *isothermal process*.

Consider an isotherm of T = 200 Celsius. At a high pressure, water is in the liquid phase. The volume of the liquid increases as the pressure drops.

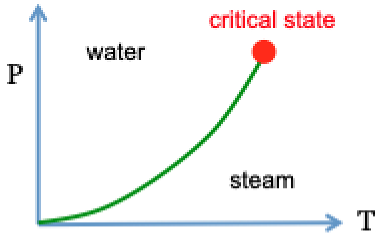


At 200 C, the NIST table (dome, temperature) lists

P = 1555 kPa
v_f = 0.001157 m^3/kg
v_g = 0.12722 m^3/kg

Temperature-pressure plane

Temperature and pressure are both intensive properties. Each point on the temperature-pressure plane represents a pair of temperature and pressure.

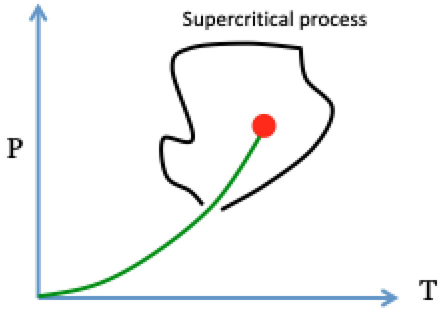


Single-phase states. When the substance equilibrates in a single-phase state, the state corresponds to a point in the temperature-pressure plane. In the vicinity of a single homogeneous state in equilibrium, the state can change continuously by independent change of temperature and pressure. All single-phase states form a continuous region.

Two-phase states. When the substance equilibrates in a two-phase state, each phase is a saturated state, and the two saturated states have the same temperature and the same pressure. In the temperature-pressure plane, all two-phase states fall on a curve, called a *phase boundary*. A point on the phase boundary represents many two-phase states, each state being a mixture of the two saturated states of some proportion. For the phase boundary, given a pressure, the steam tables list the temperature, as well as the specific volumes, energies, and entropies of the two saturated states.

Supercritical process. As the pressure increases, the liquid-gas phase boundary terminates at the critical state. Beyond the critical state, no boundary divides water and steam.

Consider a point on the liquid-gas boundary. Near the point, the substance forms a liquid on one side of the boundary, and forms a gas on the other side of the boundary. The liquid can change to the gas through a sequence of single-phase states, without crossing the liquid-gas phase boundary. Such a sequence of single-phase states is called a *supercritical process*.



Exercise. Search for a temperature-pressure phase diagram for ammonia. Ammonia can be safely stored in a tank as a liquid at room temperature. Explain the science of this practice.

Exercise. Nitrogen cannot be stored as a liquid at room temperature. Why?

Exercise. Sketch a supercritical process on a T-v diagram and on a P-v diagram.

Exercise. Wiki supercritical fluid extraction. Explain the science of this process.

Ice, water, and steam

We have just studied the two phases—water and steam. We now look at the three phases—ice, water, and steam.

Three-phase equilibrium

Fact. When ice, water, and steam equilibrate as a three-phase mixture, the three phases in the mixture have the same temperature and the same pressure:

T = 0.01 Celsius,
P = 0.611657 kPa.

In the three-phase mixture, each phase is at a particular state with the following extensive properties.

	volume m^3/kg	energy kJ/kg	entropy kJ/(kg K)
ice	0.00109	-334	-1.22
water	0.00100	0	0
steam	206.132	2375	9.16

- The energy and entropy are set to zero for the state of water in equilibrium with both ice and steam.
- Water expands by 9% on freezing.
- The specific volume of the steam in the three-phase mixture, 206.132 m^3/kg, is enormous compared to the specific volume of the steam in the two-phase mixture at 100 C, 1.6939 m^3/kg. Both are enormous compared to the specific volumes of water and ice.
- The energy of evaporation is much larger than the energy of melting.
- The entropy of evaporation is much larger than the entropy of melting.

Caution. The three-phase equilibrium is commonly called the *triple point*. This name is badly conceived. As we will see, the three-phase equilibrium appears as a point only on one thermodynamic plane, the T-P plane, but appears as a line or a triangle on all other thermodynamic planes. In the phrase “triple point”, the word “triple” is serviceable, but the word “point” is pointless and misleading.

I will use the phrase *three-phase equilibrium*, or *three-phase states*. In equilibrium, the three states of ice, water, and steam can form mixtures of any mass fractions.

Experimental observations of three-phase equilibrium

The three-phase equilibrium is commonly observed. A half bottle of water with ice demonstrates, approximately, a state of three phases in equilibrium.

Experiment 1. Cool a half bottle of water in a refrigerator, and ice forms at the expense of water and steam. Because freezing requires energy, you have plenty of time to observe that the three phases—ice, water, and steam— do equilibrate. After all water is consumed, inside the bottle is an ice-steam mixture. In this experiment, the H_2O molecules in the bottle starts in a two-phase state (water-steam of a fixed proportion), become a sequence of three-phase states (water-steam-ice of various proportions), and end in a two-phase state (ice-steam of a fixed proportion).

Experiment 2. Here is an alternative experiment. Before the class, I filled this bottle with some ice from the refrigerator in the kitchen on this floor. By now, some ice has melted into water. In the bottle, the H_2O molecules equilibrate in a three-phase state, a mixture of ice, water, and steam. The three phases can equilibrate in many states of different proportions of ice, water, and steam. For the three phases to equilibrate, I need to make sure that thermal energy in the room enters the bottle slowly, so that the three phases have the uniform temperature and pressure. Perhaps I should wrap the bottle with some cloth to slow down the transfer of energy, and to let the three phases in the bottle equilibrate.

Experiment 3. YouTube three-phase equilibrium. This experiment requires more sophisticated equipment than the above experiments, but let you watch an ice-water mixture boil.

Rule of three-phase mixture

Let m be the mass of a mixture, m_f be the mass of the water, m_g be mass of the steam, and m_s be the mass of the ice. Thus,

$m = m_f + m_g + m_s$.

Denote the mass fraction of the steam by $x = m_f/m$, and the mass fraction of the ice by $y = m_s/m$. The mass fraction of the water is $1 - x - y$.

The above table lists the specific volumes of the particular states of ice, water, and steam: v_s, v_f, and v_g. The volume of the mixture is the sum of the volumes of the three single-phase states:

$V = m_f v_f + m_g v_g + m_s v_s$.

Dividing this equation by the mass of the mixture, m, we obtain the specific volume of the mixture:

$v = (1 - x - y)v_f + xv_g + yv_s$.

This equation is called the *rule of three-phase mixture*.

Because we have set $u_f = 0$, the specific energy of the mixture is given by

$u = xu_g + yu_s$.

Similarly, because we have set $s_f = 0$, the specific entropy of the mixture is given by

$s = xs_g + ys_s$.

Exercise. 1 kg of three-phase mixture of H_2O has a volume of 100 m^3 and an energy of 1000 kJ. Determine the entropy of the mixture.

Exercise. A rigid, 1-liter bottle is filled with a half liter of water at 25 C. The other half of the bottle is filled with pure steam. The bottle is then cooled to a three-phase mixture, in which 0.25 liter is water. Determine the energy and entropy of the three-phase mixture, as well as the volume of the ice.

Water expands on freezing

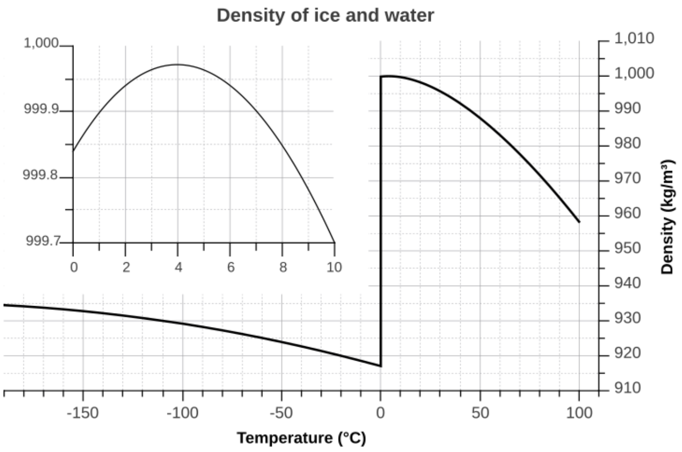
Fact. Among pure substances, H_2O is anomalous: water expands on freezing. This anomaly is of great practical and scientific importance.

Exercise. YouTube bursting water pipe. Explain the science of this demonstration.

Exercise. Fish survives in winter. YouTube why does ice float in water. Describe the molecular picture how H_2O changes volume as temperature changes.

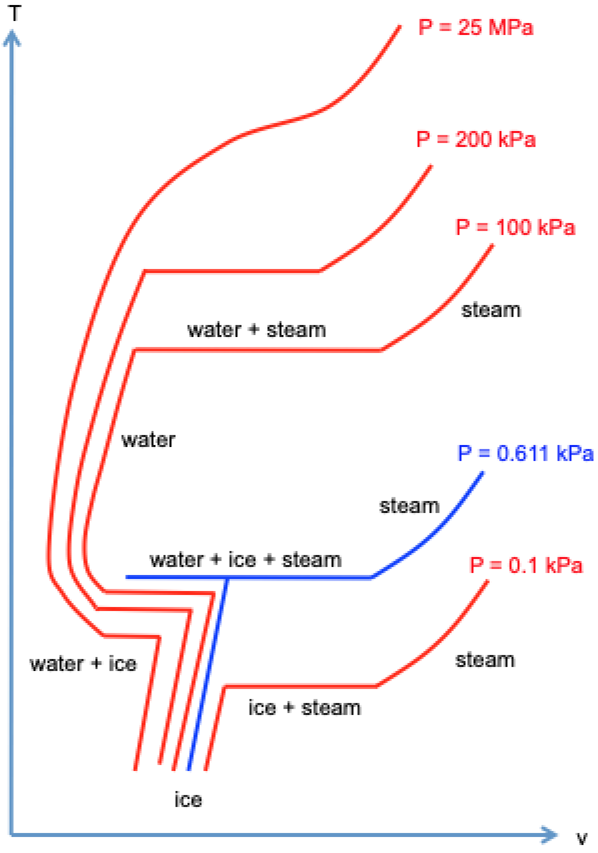
Wiki water (data page). A large collection of H_2O molecules is under a constant pressure of 100 kPa.

- Below 0 Celsius, H_2O molecules form ice. Ice expands as temperature increases. At 0 Celsius, ice melts and becomes water, and the volume contracts by about 9%.
- Above 0 Celsius, H_2O molecules form water.
- Between 0 and 4 Celsius, water contracts as temperature increases.
- Above 4 Celsius, water expands as temperature increases.



Temperature-volume plane

On the T-v plane, we draw constant-pressure curves for H_2O. For visual clarity, the curves are drawn out of scale.



Condensation. Let us follow the events when the pressure is fixed at 100 kPa. We are familiar with three segments of the constant-pressure curve: single-phase states of steam, two-phase states of steam and water, and single-phase states of water. Above 4 Celsius, water contracts on cooling. Below 4 Celsius, water expands on cooling.

Freezing. Let us continue to follow the events when the pressure is fixed at 100 kPa. Now comes the fourth segment of the constant-pressure curve. At 0 Celsius, some H_2O molecules form ice, and others remain to be water. In the two-phase states of water and ice, the water is in one fixed state, and the ice is in the other fixed state. The specific volumes of the state of water and the state of ice are

$v_f = 0.001000\ m^3/kg$,
$v_s = 0.001091\ m^3/kg$.

Water expands by 9% on freezing. During freezing, molecules transition from water to ice. The two-phase mixture expands in volume, but keeps at the constant temperature of 0 Celsius.

Finally we reach the fifth segment of the constant-pressure curve. After all H_2O molecules form ice, temperature can decrease again. The volume of the ice contracts as temperature decreases.

Sublimation. Let us follow the events when the pressure is fixed at 0.1 kPa. Below -20 Celsius, all H_2O molecules form ice. As temperature increases, the ice expands.

At -20 Celsius, ice starts to sublimate. Some H_2O molecules form steam, and others remain in the ice. In the two-phase states of ice and steam, the ice is in one fixed state, and the steam is in the other fixed state. The specific volumes of the two states are

$v_s = 0.001087\ m^3/kg$,
$v_g = 1128.113\ m^3/kg$.

The specific volume of two states differ by six orders of magnitude. During sublimation, the volume of the ice-steam mixture expands, and the temperature is fixed at -20 Celsius.

After all H_2O molecules form steam, temperature can increase again, and the volume of the steam expands.

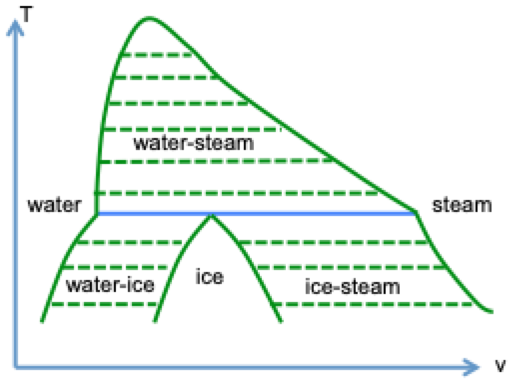
Three-phase states. The three phases—ice, water, and steam—equilibrate at 0.01 Celsius and 0.611 kPa. On the T-v diagram, the constant-pressure curve for 0.611 kPa is drawn blue. This curve results from the collision of a curve of a constant pressure slightly above 0.611 kPa, and a curve of a constant pressure slightly below 0.611 kPa.

Let us follow the events along this constant-pressure curve, 0.611 kPa. Below 0.01 Celsius, all H_2O molecules form ice. As the temperature increases, the ice expands. At 0.01 Celsius, some ice melts to form water, other ice sublimates to form steam, and still ice remains to be ice.

During this process, the volume can expand or contract, and the temperature is fixed at 0.01 Celsius. After all H_2O molecules form steam, temperature can increase again.

The constant-pressure curves make the Tv diagram look like a Christamas tree. The anomaly that ice contracts on melting gives the tree an ice trunk.

Phase diagram. On the T-v plane, we now do not draw constant-pressure curves. Instead, we mark the regions of ice, water-ice mixtures, and ice-steam mixtures, in addition to the regions of water, steam, and water-steam mixtures. Such a diagram demarcates phases, is called a *phase diagram*



The T-v diagram looks like a person with two legs, one lag being much skinnier than the other.

I draw some horizontal lines in the regions of two-phase mixtures. The water-steam transition has a critical state, and forms a dome. Neither the water-ice transition nor the ice-steam transition has critical state. The regions of these two transitions take the shapes of belts.

In total there are two regions of single phases: one for ice, and the other for water and steam. There are three regions of two-phase mixtures: the water-steam dome, the water-ice belt, and the ice-steam belt. The region of three-phase (ice-water-steam) mixtures collapses to a horizontal segment.

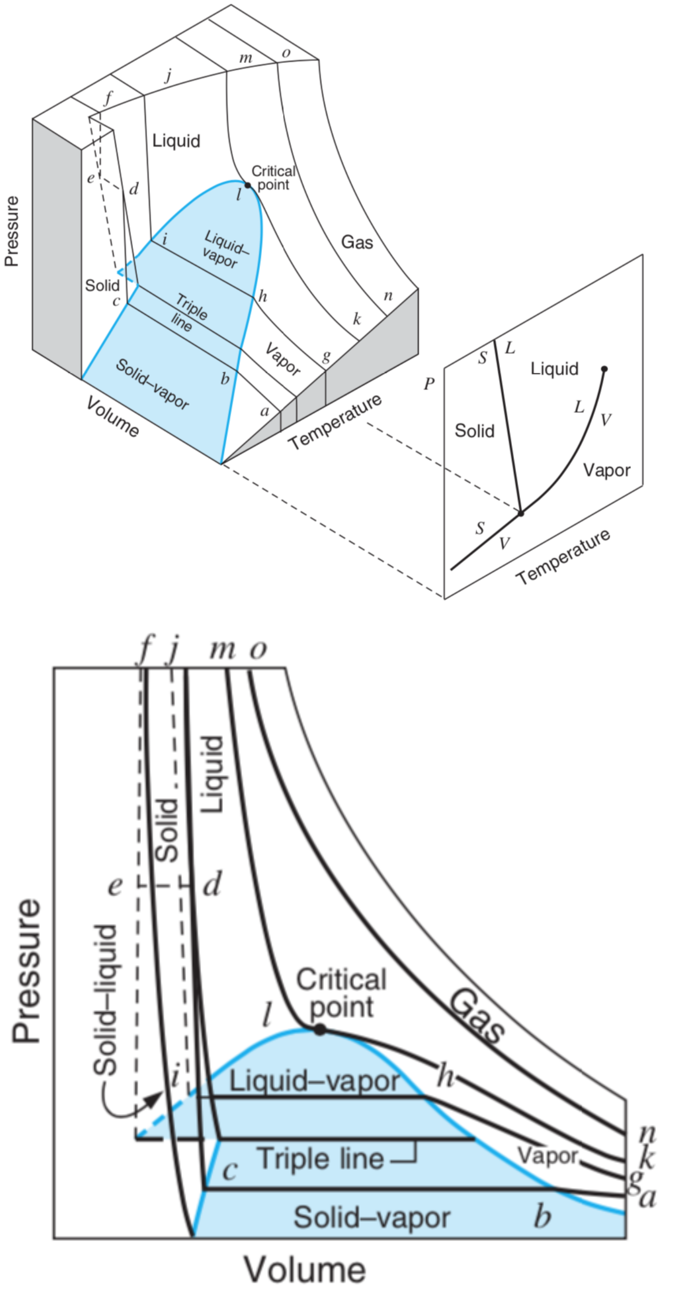
Again, the diagram is not drawn to scale. The specific volumes of ice and water are close, which are much smaller than the specific volume of steam.

Pressure-volume-temperature surface

Facts. The function P(T,v) is a surface in the pressure-volume-temperature space. In the single-phase regions, water and steam together correspond to a single smooth surface, and ice corresponds to another smooth surface.

A portion of the water-steam surface is cut out, replaced with the dome of water-steam mixtures.

The smooth water-steam surface connects to the smooth ice surface by two belts, one for water-ice mixtures, and the other for ice-steam mixtures.



(Fig. 2.7 of BS)

Fact. Inspecting the PvT surface, we note that the projection on the T-v plane does not stack surfaces. That is, each pair of values of (T,v) corresponds to one state.

Pressure-volume plane

Facts. Recall the anomaly: water expands on freezing. The specific volume of ice is larger than that of water. When you look at the PvT surface along the temperature axis, the smooth ice surface blocks the ice-liquid belt, a corner of the water-steam dome, and part of the smooth water-steam surface.

When the PvT surface of H_2O is projected on the Pv plane, the projection stacks three parts of the PvT surface on top of one another: the smooth ice surface, the ice-water belt, and the smooth water-steam surface and part of the water-steam dome. The stack of these surfaces makes the Pv diagram look intricate. In the stacked region, each pair of values (P,v) correspond to three states. This multivaluedness has not stopped P and v from being a popular pair of independent properties. Of course, the multivaluedness disappears when we are only look at water and steam.

The Pv diagram looks like a gymnast, the skinny leg up.

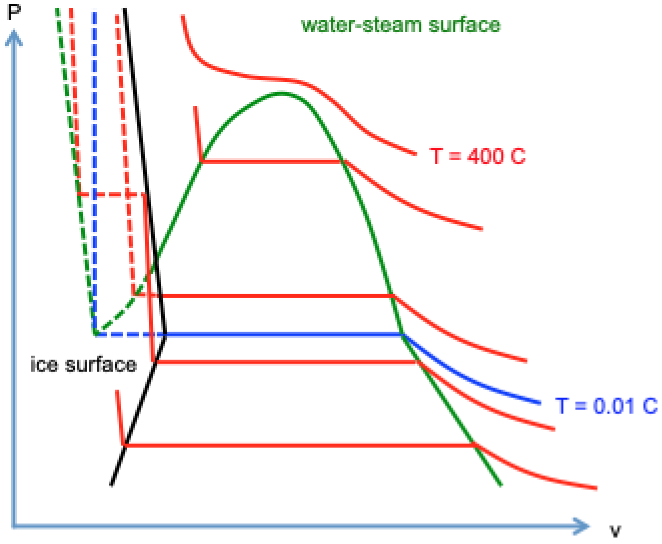
Let us follow the events along the isotherm abcdef.

- ab. Steam increases pressure.
- bc. Ice forms at the expense of the steam, and the pressure is constant.
- cd. Ice increases pressure.
- de. Ice melts into water, and the pressure is constant.
- ef. Water increases pressure.

Let us follow the events along the isotherm ghij.

- gh. Steam increases pressure
- hi. Steam condenses into water, and the pressure is constant.
- ij. Water increases pressure.

In the following sketch, I mark the isotherm of 0.01 C blue, the boundary of the smooth water-steam surface green, and the boundary of the smooth ice surface black. I mark isotherms red. The water-steam dome, ice-steam belt, and ice-water belt are all marked with horizontal isotherms in red.



Temperature-pressure plane

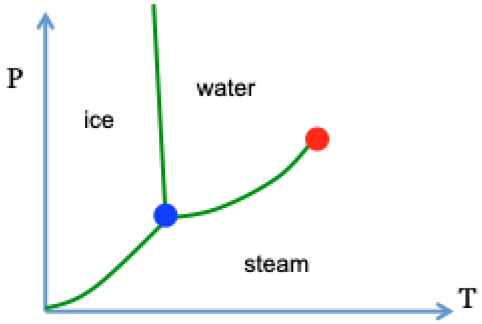
Both temperature and pressure are intensive properties. In the temperature-pressure plane, we mark the three-phase equilibrium, critical state, and phase boundaries. There are three two-phase phase boundaries: water-steam, water-ice, and ice-steam.

Single-phase regions. The single-phase states of water and steam form a continuous region. The single-phase states of ice form a region, which is separated from the single-phase region of water and steam by two boundaries. We will ignore many phases of ice at high pressure. See phase diagram of water.

Water-steam boundary. The water-steam dome in the T-v plane collapses into the water-steam boundary in the T-P plane. Each point on the boundary corresponds to many water-steam mixtures of various mass fractions. The boundary terminates at the critical state on one end, and the three-phase equilibrium on the other end. There is no boundary beyond the critical point.

Water-ice boundary. The water-ice belt in the T-v plane collapses into the water-ice boundary in the T-P plane. Each point on the boundary corresponds to many water-ice mixtures of various mass fractions. The water-ice boundary terminates at the three-phase equilibrium, but does not have a critical point. The water-ice boundary is nearly a straight line, with a negative slope about - 13 MPa/K. As we will see later, the negative slope of the water-ice boundary relates to that water expands on freezing.

Ice-steam boundary. The ice-steam belt in the T-v plane collapses into the ice-steam boundary in the T-P plane. Each point on the boundary corresponds to many ice-steam mixtures of various mass fractions. The ice-steam boundary terminates at the three-phase equilibrium, but does not have a critical point.



Three-phase equilibrium (triple point). When the substance equilibrates in three-phase states, the three phases have the same temperature and the same pressure. In the temperature-pressure plane, all the three-phase states states collapse to a single point, the three-phase equilibrium. YouTube three-phase equilibrium.

Thus, the three-phase equilibrium is *not* a single state, but represents many states. Each state is a mixture of the three phases of some proportions.

Exercise. Sketch several constant-temperature curves on the pressure-volume plane around the critical state and around the states in which ice, water, and steam coexist in equilibrium.

Exercise. On the temperature-entropy plane, sketch the regions of ice, water, and steam, along with the regions of mixtures of two phases, and the region of mixtures of three phases. Find in a steam table (or elsewhere) the values of temperature and entropy at the critical state and at the three-phase coexistence. Mark these values in your sketch. Write a few sentences for each region.

Exercise. 1 kg of H_2O molecules is found to be a mixture of the three phases in equilibrium, of volume 100 m^3 and energy 500 kJ. What is the entropy of the mixture?

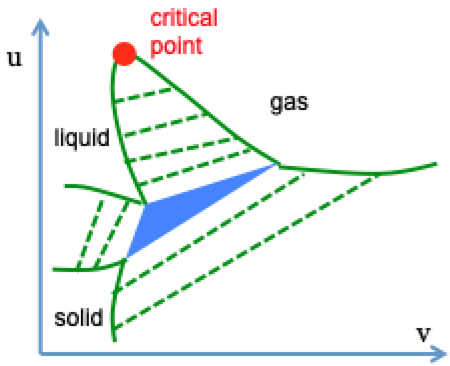
Energy-volume plane

Both energy and volume are extensive properties, so that each state corresponds to a distinct point in the energy-volume plane.

The single-phase states of water and steam form a connected region. The single-phase states of ice form a region. The two-phase states of water-steam mixtures form a dome. The two-phrase states water-ice mixtures form a belt, and the two-phase states of ice-steam mixtures form another belt. The three-phase states of ice-steam-water mixtures form a triangle.

Inside each region of two-phase mixtures are tie lines that connect the states of the two phase in equilibrium. A state of mixture corresponds to a point on the tie line, and is determined by the rule of two-phase mixture.

For the three-phase mixtures, the states of the three phases in equilibrium correspond to the three corners of the triangle. A state of mixture corresponds to a point in the triangle, and is determined by the rule of two-phase mixture.



I do not draw the sketch with the anomaly of H_2O. Here I draw the “normal” behavior of many substances, in which liquid contracts on freezing. Also, the volume of gas is enormous compared to the volumes of solid and liquid. To fit the triangle in the diagram, I draw out of scale.

Exercise. Find the data to draw the phase diagram of H_2O on the energy-entropy plane. Include the water-steam dome, critical state, ice-steam belt, ice-water belt, ice-water-steam triangle, as well as the region of single-phase states of ice, and the region of single-phase states of water and steam. Include several tie lines in each region of two-phase states.

Three types of thermodynamic planes

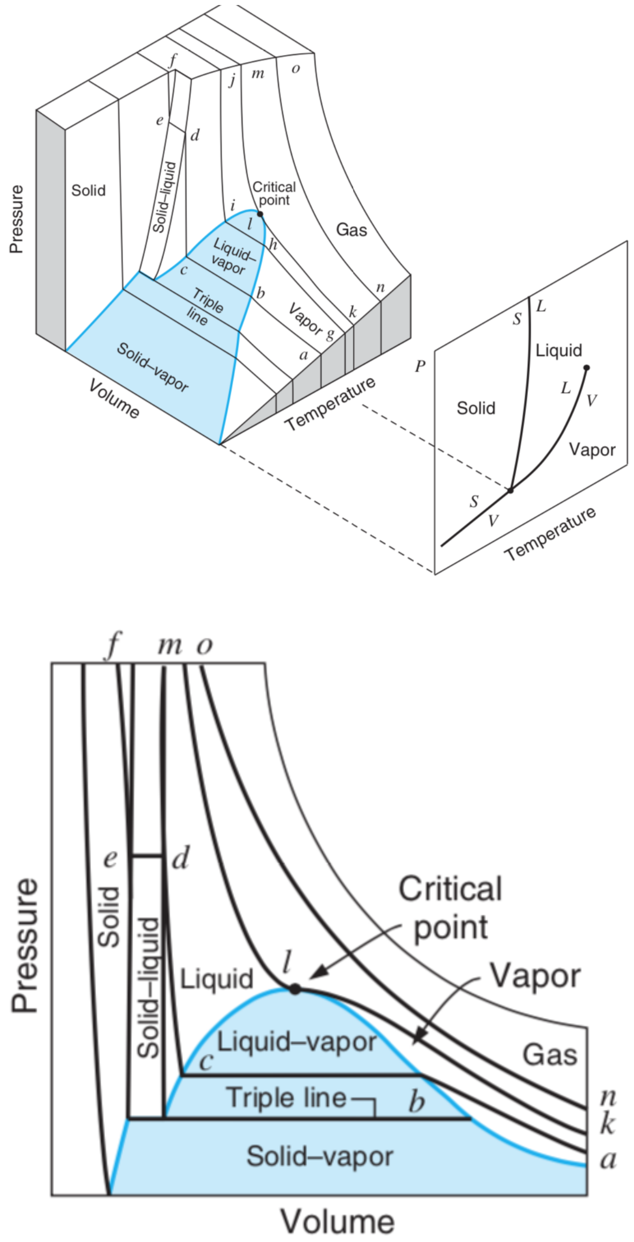
Fact. Both T and P are intensive properties, but V is an extensive property. When two phases equilibrate, T is uniform in the mixture, and so is P. But the specific volume v obeys the rule of mixture. Consequently, the T-P diagram and the T-v diagram have different topologies. The dome on the T-v plane collapses to the phase boundary on T-P plane.

The T-v and P-v diagrams have the same topology. The u-v diagram has a topology different from that of T-P and that of T-v.

We classify thermodynamic planes into three types: intensive-intensive, intensive-extensive, and extensive-extensive. There is only one intensive-intensive plane in common use: the TP plane. There are many intensive-extensive planes in common use. A popular extensive-extensive plane is the enthalpy-entropy plane.

Three phases of carbon dioxide

Like most other substances, liquid carbon dioxide contracts on freezing. No part of the PvT surface blocks other parts of the surface. The PvT surface consists of the solid surface, liquid-gas surface, liquid-gas dome, solid-gas belt, and liquid-solid belt. To be consistent, the solid-liquid belt should also be shaded blue.



(Fig. 2.8 of BS)

Exercise. Follow the isotherm abcdef on the Pv plane, and interpret the events.

Exercise. Carbon dioxide expands on melting. Sketch several constant-pressure curves on the temperature-volume plane around the critical state and around the three-phase states.

Exercise. Sketch the three-phase diagram of carbon dioxide on the temperature-entropy plane.

Entropy

These concrete examples have reminded us of many empirical facts. We can go on to describe a lot more examples. But the large number of examples prompt a question: do they tell us a unifying principle?

Here enters the leading role of the play—entropy.

Fact. Entropy is a thermodynamic property. Steam tables list measured values of entropy of H_2O in various states, along with values of temperature, pressure, volume, and energy. What gets measured gets used.

Fact. The definition of entropy requires two ideas: isolated system and sample space.

Isolated system

System. We have met the cast. Now look at the stage—the *world*. Any part of the world is called a *system*. The rest of the world is called the *surroundings*.

We can regard any part of the world as a system. Even the empty space can be a system; the vacuum hosts electromagnetic field.

A proton and an electron constitute a system, called a hydrogen atom.

A half bottle of water is a system. The system is composed of water molecules and some other molecules, such as nitrogen, oxygen, and carbon dioxide. In the half bottle of water, liquid occupies some volume, and gas fills the rest. The liquid and the gas together constitute the system.

Do we include the plastic bottle as a part of the system? Maybe, if we decide to study the permeation of water molecules through the plastic. The decision is ours.

A system and its surroundings interact in many ways. The hydrogen atom changes the shape of its electron cloud when the atom absorbs or emits photons, or when the atom is subject to an electric field.

I hold a half bottle of water in my hand. I see water because the liquid-gas interface refracts light. I shake the bottle and hear the sound. I warm up water because the vibration of the molecules in my hand couples the vibration of the molecules in water. Upon opening the bottle, I feel moist because molecules hit me. When I drink from the bottle, the bottle transfers molecules to my body. I pour honey into water and watch them mix.

Isolated system. Our play—thermodynamics—shows all modes of interaction between a system and its surroundings. But our play begins with something simpler: an *isolated system*—a system that does not interact with its surroundings.

To make the half bottle of water an isolated system, I cap the bottle to prevent molecules from leaking in and out. I insulate the bottle in a thermos to block the vibration of the molecules in my hand from coupling with the vibration of molecules in the water. I make the bottle rigid to fix the volume. I do not shake the bottle. I am alert to any other modes of interaction between the water and the surroundings. Does the magnetic field of the earth affect the water? If it does, I will find a way to shield the bottle of water from the magnetic field also.

Of course, nothing is perfectly isolated. Like any idealization, the isolated system is a useful approximation of the reality, so long as the interaction between the system and the rest of the world negligibly affects a phenomenon that I choose to study. For example, it may be too much trouble for me to isolate the water from gravity. Few people care to study water under the zero-gravity condition. Gravity is important if I move the bottle around, but unimportant if I study the pressure of the gas in the bottle.

Exercise. Describe a system and what you need to do to make it an isolated system.

Sample space

Sample space in probability. In probability, each trial of an experiment is assumed to result in one of multiple possible outcomes. Each possible outcome is called a *sample point*. All possible outcomes of the experiment form a set, called the *sample space*.

A throw of a coin is an experiment of two possible outcomes: head and tail. They are the sample points that constitute the sample space of the experiment, {head, tail}.

The notion of sample space in probability came from Mises (1919), before he came to Harvard.

Exercise. What is the sample space of a throw of a die? What is the sample space of throw a coin and a die simultaneously? What is the sample space of a throw of two dies simultaneously? How many possible outcomes do you get when you throw 1000 dies?

Quantum states of an isolated system. When a hydrogen atom is isolated at the second energy level, the isolated system has eight quantum states.

Quantum mechanics governs all systems, however complicated. A quantum state of the half bottle of water is a cloud of electrons and positions of nuclei. Such a macroscopic isolated system has a large, but finite, number of quantum states.

Quantum mechanics was started by Planck in 1900, who was a thermodynamicist and wrote a textbook on thermodynamics.

Sample space of an isolated system. An isolated system is an "experiment" in the sense of the word used in probability. The isolated system flips from one quantum state to another, rapidly and ceaselessly. Each quantum state is a possible outcome, or a sample point, of the isolated system. All the quantum states of the isolated system constitute a set, called the *sample space of the isolated system*.

The size of a sample space. Let Ω be the number of quantum states of an isolated system. The number Ω measures the size of the sample space of the isolated system.

We will soon learn the experiments that "count" the number of quantum states of a given isolated system. For now, let us meet the data—the numbers of quantum states in several familiar isolated systems.

Exercise. What is the sample space of a hydrogen atom isolated at the second energy level? Sketch the electron clouds of the individual quantum states. Wiki atomic orbital.

Nobel lecture. Schrodinger, The fundamental idea of wave mechanics, 1933.

Definition of entropy

Let Ω be the number of quantum states of an isolated system. Define the *entropy* of the isolated system by (Boltzmann 1877)

$S = \log \Omega$.

Logarithm of any base will do. For convenience, we will use the natural base e. The number e simplifies the derivative of logarithm. Recall a fact of calculus: $d \log x / dx = 1/x$. For any other base b, recall that $\log_b x = (\log_b e)(\log_e x)$, so that $d \log_b x = (\log_b e)/x$. The prefactor clutters the formula and serves no purpose.

For example, the entropy for a hydrogen atom isolated at the second energy level is log 8 = 2.079, a pure number. (Incidentally, I calculate this number by entering "In 8" in the google search box).

Caution. In explaining entropy, many books use the word “disorder”. The word explains nothing. Entropy is a well-defined, measurable property, and needs no help from an undefined, nebulous notion like “disorder”. Delete all sentences that contain the word “disorder”, and you miss nothing.

People also use the word entropy to mean disorder. “This committee is full of entropy, but has no energy!” Such usage colors conversation, but does not enhance communication. Entropy is a precise and measurable quantity. Disorder is not.

Let us remove all embellishments and focus on what entropy is: the logarithm of the number of quantum states of an isolated system. No more, no less.

Entropy is a thermodynamic property

An isolated system has a fixed number of quantum states—that is, the number of quantum states is a thermodynamic property of the isolated system. So is entropy.

Indeed, entropy is an extensive, dimensionless, and absolute property. We next examine these attributes one by one.

Entropy is extensive

Why do we hide Ω behind a log?

Two separately isolated systems. Consider two isolated systems, A and B. Isolated system A has one sample space of Ω_A quantum states, labeled as

$\{a_1, a_2,..., a_{\Omega A}\}$.

Isolated system B has another sample space of Ω_B quantum states, labeled as

$\{b_1, b_2,..., b_{\Omega B}\}$.

The two systems are *separately isolated*. Together they constitute a *composite*, which is also an isolated system. Each quantum state of this composite is a combination of a quantum state of one isolated system, a_i, and a quantum state of the other isolated system, b_j. All such combinations together constitute the sample space of the composite. The total number of all such combinations is the product:

$\Omega_{composite} = \Omega_A\Omega_B$.

Turn a product to a sum. Recall a property of logarithm:

$\log(\Omega_A \Omega_B) = \log \Omega_A + \log \Omega_B$.

Thus, the entropy of a composite of two separately isolated systems is the sum of the entropies of the two individual isolated systems.

We now see the significance of logarithm: it turns a product to a sum. The entropy of a system is the sum of the entropies of its parts, each part being separately isolated. Such an additive quantity is an *extensive quantity*.

Exercise. In defining entropy, we need a function that obeys $f(xy) = f(x) + f(y)$. Show that the logarithm is the only candidate.

Entropy is dimensionless

Fact. By definition, $S = \log \Omega$, entropy is *dimensionless*.

Fake unit. By a historical accident, however, entropy is given a unit, Joule/Kelvin. People write

$S = k_B \log \Omega$.

Here $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. As we will see, this practice comes from changing the unit of temperature from Joule to Kelvin. This change of unit for temperature leads to a fake unit for entropy: Joule/Kelvin. If we report entropy S in this fake unit, only the ratio S/k can enter any fundamental result. Nature is indifferent to our choice of a fake unit.

Caution. As we have noted before, the Boltzmann constant does no honor to the three scientists who helped to create the great play. The constant k clutters fundamental equations. Worse, the fake unit, Joule/Kelvin, gives an impression that the concept of entropy depends on the concepts of energy and temperature. This impression is wrong. As we will see, entropy and energy are two independent properties, and temperature is the child of the union of entropy and energy.

Exercise. Wiki Boltzmann constant. Describe the history of the fake unit, J/K.

Entropy is absolute

Fact. By definition, $S = \log \Omega$, zero entropy is not something arbitrary, but has empirical significance. Zero entropy corresponds to an isolated system of a single quantum state. Like volume, entropy is absolute.

Needless reference. Many tables list entropies of a pure substance at various states relative to the entropy of the substance at a particular state, called the reference state.

This practice has no merit. We tolerate relative entropy because some applications involve the change of entropy from one state to another. As we will see, certain applications require absolute entropy.

Indeed, we would be upset if relative volumes were tabulated instead of absolute volumes. Why should we tolerate relative entropies?

Nobel lecture. Nernst, Studies in chemical thermodynamics, 1921.

Absolute, dimensionless entropies per molecule of H_2O at various thermodynamic states

Busywork. The great play offers a clean definition, $S = \log \Omega$, but then thrusts upon us a fake unit and a needless reference. They are blemishes of the great play. They cause busywork. May the busywork annoy you, but not harm you. To make sure that you are annoyed, I write this section.

Absolute, dimensionless entropy per molecule in the water at 25 Celsius and 100 kPa. Water at 25 Celsius and 100 kPa has an absolute entropy of 69.950 $JK^{-1}mol^{-1}$. We next covert this fake-unit entropy to dimensionless entropy.

Let Ω be the number of quantum states per molecule. In the fake unit, J/K, the entropy per molecule is $k_B \log \Omega$. The fake-unit entropy per mole is $N_A k_B \log \Omega$. Recall that $N_A k_B = 8.314$ $JK^{-1}mol^{-1}$. Thus,

$\log \Omega = (69.956\ JK^{-1}mol^{-1})/(8.314\ JK^{-1}mol^{-1}) = 8.414$.

This value is the absolute, dimensionless entropy per molecule in water at 25 Celsius and 100 kPa.

In general, entropy in the fake unit of $JK^{-1}mol^{-1}$ is converted to dimensionless entropy per molecule by dividing the universal gas constant, $R = 8.314\ JK^{-1}mol^{-1}$. That is, R is the factor of conversion between a fake-unit entropy per mole and dimensionless entropy per molecule.

Absolute, dimensionless entropy per molecule in the water at three-phase equilibrium. For the state of water at three-phase equilibrium, the NIST steam table sets the entropy to be zero. For H_2O at 25 Celsius and 100 kPa, the table lists a relative entropy of 0.36722 kJ/kg-K. How do we convert relative, fake-unit entropy to absolute, dimensionless entropy per molecule?

The molar mass of H_2O is M = 18 g/mol. The relative, dimensionless entropy per molecule at 25 Celsius and 100 kPa is

(0.36722 J/g-K)(18 g/mol)/(8.314 $JK^{-1}mol^{-1}$) = 0.795.

In general, entropy in the fake unit of $JK^{-1}g^{-1}$ is converted to dimensionless entropy by dividing the specific gas constant, N_Ak/M. The specific gas constant for water is N_Ak/M = (8.314 $JK^{-1}mol^{-1}$)/(18 g/mol) = 0.46 $JK^{-1}g^{-1}$. That is, R/M is the factor of conversion between a fake-unit entropy per unit mass and dimensionless entropy per molecule.

For water at 25 Celsius and 100 kPa, the absolute, dimensionless entropy per molecule is 8.414, and the relative, dimensionless entropy per molecule is 0.795. Their difference is

8.414 - 0.795 = 7.619.

Recall that (absolute entropy at state A) = (relative entropy at state A) + (absolute entropy of the water at the three-phase equilibrium). Thus, 7.619 is the absolute, dimensionless entropy per molecule of the water at three-phase equilibrium.

Absolute entropy in fake unit. The state of water at three-phase equilibrium has an absolute entropy of 3.519 kJ/kg-K in the fake unit. By convention, most steam tables set the entropy at this state to be zero, and list entries in other states relative to this reference. To convert the relative entropies in the steam tables to absolute entropies, simply add 3.519 kJ/kg-K to every entry.

Absolute, dimensionless entropy per molecule in the ice at three-phase equilibrium. For the ice at the three-phase equilibrium, Table B.1.5 of the textbook lists an entropy of - 1.221 J/g-K. This is a relative, fake-unit entropy.

At this state, the dimensionless relative entropy per molecule is

(- 1.221 J/g-K)(18 g/mol)/(8.314 $JK^{-1}mol^{-1}$) = - 2.643.

At three-phase equilibrium, when a molecule transitions from ice to water, the dimensionless entropy increases by 2.643, which is called the *entropy of melting*.

The dimensionless absolute entropy per molecule of the ice at the three-phase equilibrium is

- 2.643 + 7.619 = 4.976.

Absolute, dimensionless entropy per molecules in the steam at three-phase equilibrium. For the steam at the three-phase equilibrium, Table B.1.5 lists a relative entropy of 9.156 J/g-K.

At this state, the dimensionless relative entropy per molecule is

(9.156 J/g-K)(18 g/mol)/(8.314 $JK^{-1}mol^{-1}$) = 19.823.

At the water-ice-steam equilibrium, when a molecule transitions from ice to steam, the dimensionless entropy increases by

19.823 - (-2.643) = 22.466.

This value is called the *entropy of sublimation*.

The dimensionless absolute entropy per molecule of the steam at the three-phase equilibrium is

19.823 + 7.619 = 27.442.

Numbers of quantum states per molecule in ice, water, and steam

Ice, water, steam in the three-phase equilibrium. I list below the absolute, dimensionless entropies per molecule in the ice, water, and steam at the three-phase equilibrium.

	relative entropy kJ/(kg-K)	absolute entropy kJ/(kg-K)	absolute entropy dimensionless	Number of quantum states Ω
ice	- 1.221	2.298	4.976	144.89
water	0	3.519	7.619	2036.52
steam	9.156	12.68	27.44	8.11×10^{11}

Also listed are the relative and absolute entropies in the fake unit, kJ/(kg-K). Note the procedures of conversion:

- (absolute entropy at state A) = (relative entropy at state A) + (absolute entropy of the water at the three-phase equilibrium).
- (entropy in kJ/kg-K) = (dimensionless entropy)(specific gas constant). The specific gas constant for H_2O is R/M = (8.314 J/mol-K)/(18 g/mol) = 0.46 kJ/kg-K.

Fact. The following two functions are inverse to each other.

y = log x,
x = exp y.

Number of quantum states per molecule. Recall the definition of the absolute, dimensionless entropy, S = log Ω. Given the absolute, dimensionless entropy per molecule in a state of a substance, the number of quantum states per molecule is

$\Omega = \exp(S)$.

For water at 25 Celsius and 100 kPa, the absolute, dimensionless entropy per molecule is 8.414, so that the number of quantum states per molecule is

$\Omega = \exp(8.414) = 4509.76$.

I do not have an intuition about this enormous number of quantum states per molecule for water at 25 Celsius and 100 kPa. But let me develop some intuition by comparing this number with numbers of quantum states at other thermodynamic states of H_2O.

For this purpose, I list the numbers of quantum states per molecule in the states of ice, water, and steam in three-phase equilibrium. The trend is consistent with my expectations. In the ice, the molecules form a lattice and can not freely translate and rotate, giving a small number of quantum states. In the water, the molecules can translate and rotate, but still touch one another, giving a larger number of quantum states. In the steam, the molecules can fly, giving the largest number of quantum states: almost a trillion quantum states per molecule.

At 25 Celsius and 100 kPa, water has 4509.76 quantum states per molecule. In three-phrase equilibrium, water has 2036.52 quantum states per molecule. The change in the number of quantum states is modest when a substance changes thermodynamic state within the same phase.

Exercise. Calculate the number of quantum states per CO_2 molecule in each phase at the three-phase equilibrium. List the references where you find the data needed for the calculation.

Exercise. Graphite is a form of carbon. At 25 Celsius and 100 kPa, the absolute entropy of graphite is 5.740 kJ/K-kmol. How many quantum states per carbon atom are in the graphite?

Exercise. Carbon atoms can also aggregate in other forms, such as diamond, graphene, nanotube, and buckyball. Learn about these forms online, and find the entropy per carbon atom in each form.

Energy, space, matter, charge

Now enters the supporting actors—energy, space, matter, and charge. These supporting roles are equally important in thermodynamics.

We have already looked at space in terms of length, area, and volume. In dispersion of ink, the volume in which pigment particles are confined acts as an internal variable.

We have also looked at matter in terms of molecules, electrons, and protons. In a half bottle of water, the number of molecules in the gas acts as an internal variable.

Now let us watch energy act.

Potential energy

An apple weighs about 1 Newton. When I pick up the apple from the ground, the apple reaches about 1 meter high and adds about 1 Joule of energy. This form of energy is called potential *energy* (PE). From mechanics you have learned the fact:

PE = (weight)(height).

Potential energy has the unit of force times length, (Newton)(meter). This unit of energy is called the Joule.

The height is relative to some fixed point, such as the ground. Thus, potential energy is a *relative quantity*. For a given height, the potential energy is proportional to the amount of material. Thus, potential energy is also an *extensive quantity*.

From mechanics you have learned another fact:

weight = (mass)(acceleration of gravity).

An apple has a mass about 0.1 kg. The acceleration of gravity is about 10 m/s^2. Thus, the weight of the apple is (0.1 kg)(10 m/s^2) = 1 Newton.

Definition of energy

Energy is whatever that can lift a weight to some height. By this definition, energy is conserved, relative, and extensive.

This definition of energy makes the principle of the conservation of energy a self-fulfilling prophecy. The definition calls for action. It is up to people to discover energy in its various forms, and invent ways to convert energy from one form to another. How do we know that something offers a form of energy? Just test if this something can lift a weight to some height.

Kinetic energy

My hand now releases the apple. Just after the release, the apple is 1 meter high and has zero velocity. The falling apple then loses height, but gains velocity. The energy associated with the velocity of a mass is called the *kinetic energy* (KE). The falling apple *convert* potential energy to kinetic energy. Mechanics tells us that

KE = (½)(mass)$(\text{velocity})^2$.

The conservation of mechanical energy. The friction between the apple and the air is negligible. Mechanics tells you that, as the apple falls, the sum of the potential energy and the kinetic energy is constant—that is,

PE + KE = constant.

The potential energy and kinetic energy are two forms of *mechanical energy*. The above equation says that mechanical energy is *conserved* when friction is negligible.

Exercise. What is the velocity of the apple just before hitting the ground?

Exercise. A tiger jumps 1 m high. What is the velocity of the tiger just before it hits the ground?

Exercise. Derive the conservation of potential and kinetic energy from Newton's second law.

Exercise. The word *energy* was first used as a scientific term by Thomas Young (1807), in A Course of Lectures on Natural Philosophy and the Mechanical Arts. He wrote, "The term energy may be applied, with great propriety, to the product of the mass or weight of a body, into the square of the number expressing its velocity." His definition differs by a factor of ½ from the modern definition of kinetic energy. Explain why we need the factor of ½.

Thermal energy (internal energy)

An apple falls from a height, and gains a velocity just before hitting the ground. After hitting the ground, the apple bumps, rolls, and then stops. What happens to all that potential energy and kinetic energy?

Just before the apple hits the ground, all the potential energy has converted to the kinetic energy. After the apple hits the ground and comes to rest, all the kinetic energy of the apple disperses, or *dissipates*, into the interaction and movement of the molecules inside the apple and the ground. We say that the apple and the ground gain *thermal energy* (TE), also called *internal energy*. We generalize the principle of the conservation of energy to

TE + PE + KE = constant.

The word *thermal* is an adjective associated with microscopic interaction and movement. Thermal energy is just the potential energy and kinetic energy at microscopic scale. We designate PE and KE as the potential energy and kinetic energy at macroscopic scale.

Thermal energy of pure substance. Thermal energy is a thermodynamic property. Thermal energies of water and steam in various thermodynamic states are listed in the steam tables. Thermal energy is a relative property. In steam tables, it is common to set the thermal energy to be zero for the water at the three-phase equilibrium.

At 100 kPa, water boils at about 100 Celsius. On boiling, H_2O molecules form a mixture of two states: the state of water has a specific energy of u_f = 417.33 kJ/kg, and the state of steam has a specific energy of u_g = 2506.06 kJ/kg. The the difference defines the *energy of phase change*, u_{fg} = 2088.72 kJ/kg.

Thermal energy is an extensive property. Thus, the specific thermal energy in a mixture of water and steam obeys the rule of mixture:

$u = (1 - x)u_f + xu_g$.

Caution. In old literature, the word *heat* was often used as a synonym for thermal energy. In modern usage in thermodynamics, heat means a method to transfer energy. The two concepts—heat and thermal energy—are distinct. We can increase the thermal energy of a half bottle of water by transferring energy by heat, e.g., by placing the bottle over a fire. We can also increase the thermal energy of the half bottle of water without transferring energy by heat; we can simply shake the bottle.

Exercise. 2 kg of H_2O is heated from a state of (25 Celsius, 100 kPa) to a state of (80 Celsius, 200 kPa). Use a steam stable to find the change in internal energy.

Incidentally, Benjamin Thompson, Count Rumford, a pioneer in the investigation of thermal energy, was born in 1753, in Woburn, Massachusetts.

Electrical energy

Electric charge. This course will only deal with two species of charged particles: electrons and protons. Every electron has the same charge, called the negative charge. Every proton has the same charge, called the positive charge. The magnitude of the two types of charges is the same, denoted by e. Thus, e is the Nature's unit for charge.

The principle of the conservation of charge is just the conservation of the number of electrons and the conservation of the number of protons.

A human's unit for charge is coulomb. The 2019 redefinition of the SI base units defines the conversion factor between the two units of charge:

$e = 1.602176634 \times 10^{-19}$ coulomb.

In practical calculations, take $e = 1.6 \times 10^{-19}$ coulomb.

Voltage. Voltage is defined by

Change in energy = (voltage)(change in amount of charge).

When the charge is measured in the unit of the number of electrons and protons, the unit of voltage is the same as energy, Joule. When the charge is measured in the unit of coulomb, the unit of voltage is called volt. The conversion factor of the two units of voltage is

1 volt = 1.6×10^{-19} Joule.

Electrical energy. Electrical energy (EE) takes many forms. One way to use electrical energy is the resistive heating. A voltage of an electric outlet moves electrons in a metal wire, and the resistance of the metal converts the electrical energy into thermal energy. Recall Ohm's law:

voltage = (resistance)(current).

The electrical energy is

EE = (resistance)$(\text{current})^2$(time) = (voltage)(current)(time).

Chemical energy

Chemical reaction. Chemical energy (CE) has always been familiar to humans in the form of fire and food. Chemical energy acts during chemical reaction. In a fire, a fuel reacts with oxygen in air. An animal converts food to the movement of muscles. These chemical reactions are rather complicated. Let us illustrate chemical energy by looking at a simple chemical reaction.

At atmospheric pressure, above 100 degree Celsius, water molecules form a gas. At this pressure and temperature, oxygen molecules also form a gas, so do hydrogen molecules. When the three species of molecules are enclosed in the same container, molecules fly and collide. After collision, two molecules separate on some occasions, but form new molecules on other occasions. Let us focus on the chemical reaction

$O_2 + 2H_2 = 2H_2O$.

Each oxygen molecule consists of two oxygen atoms, each hydrogen molecule consists of two hydrogen atoms, and each water molecule consists of two hydrogen atoms and one oxygen atom. In this reaction, the oxygen molecules and hydrogen molecules are called the *reactants*, and the water molecules are called the *products*.

A chemical reaction does not change the number of each species of atoms, but changes the number of each species of molecules.

Energy of reaction. Chemical energy is stored in chemical bonds between atoms in molecules. The value of energy depends on the molecule. A rule of thumb is that each chemical bond has energy on the order of 1 eV, which means 1.6×10^{-19} J.

Consider a cylinder of a fixed volume, immersed in a large tank of water. When a chemical reaction takes place inside the cylinder, the tank either gains or loses thermal energy. The change in thermal energy defines the *energy of reaction*.

Exercise. Describe how one can test if electrostatics offers a form of energy.

Exercise. Find the nutrition energy of a banana. If this nutrition energy is fully converted to the potential energy of the banana, what will be the height of the banana?

Energy belongs to many sciences

Energy plays parts in many sciences. All have much to claim about energy: forms of energy, stores of energy, carriers of energy, conversion of energy from one form to another, and flow of energy from one place to another.

Associated with these words—forms, stores, carriers, conversion, and flow—are a great variety of inventions and discoveries. Examples include fire, food, blood, wind, rivers, springs, capacitors, water wheels, windmills, steam engines, refrigerators, turbines, generators, batteries, light bulbs, and solar cells. These you have learned, and will learn more, from many courses (including this one), as well as from daily life. These facts do not originate from thermodynamics, but we will use them just as we use facts in physics, chemistry, and calculus. We do not steal lines from other sciences; we borrow.

It has been common to let the supporting actor—energy—to dominate the play of thermodynamics. Energy is a particular energetic actor, apt to instigate commotion that easily diverts our attention from the leading role of the play—entropy. We have no time for this diversion. We will let energy play its supporting role, along with space, matter, and charge.

	to thermal	to mechanical	to electrical	to chemical
thermal	heat exchanger	engine	thermocouple	reaction
mechanical	friction	turbine	generator	fracture
electrical	resistor	compressor	capacitor	charging battery

chemical	fire, food	muscle	battery	reaction

Exercise. YouTube Stirling engine. Here is the instruction sheet of the Stirling engine that I brought to the class. Explain how this engine works.

Exercise. Use your phone to show the Sankey diagram and energy flow charts to a friend outside the class. Write a few sentences to summarize your conversation. Take a look at the website of energy flow charts. Compare, and comment on, the energy flow charts of China and India.

Exercise. What is the function of a turbine? How does it work? Link your answer to a video online.

Exercise. What is the function of a compressor? How does it work? Link your answer to a video online.

Exercise. What is the function of a generator? How does it work? Link your answer to a video online.

An isolated system conserves energy, space, matter, and charge

Beside energy, we now look at the other supporting roles: space, matter, and charge.

I make a half bottle of water into an isolated system. I close the bottle so that water molecules can neither enter nor leave the bottle. I thermally insulate the bottle to stop any energy transfer by heat. I do not squeeze the bottle, so that the volume of the bottle is fixed. There is also no transfer of charge between the system and its surroundings.

We state the *principles of conservation*:

An isolated system conserves energy, space, matter, and charge.

Exercise. Energy is liberated when hydrogen and oxygen explode. Does this observation violate the principle of the conservation of energy?

Exercise. Energy is liberated when water freezes. Does this observation violate the principle of the conservation of energy?

Exercise. Can you cool a kitchen by opening the door of a refrigerator?

Exercise. What are space, matter, and charge? Do you know why each is conserved?

Exercise. Baby Lucas has discovered a fact: the number of people that enter a room equals the change in the number of people in the room plus the number of people that leave the room. Explain this fact to baby Lucas. Will the phrase “the law of the conservation of the number of people” be useful in your explanation?

Exercise. Watch the Feynman Lecture on Conservation Principles. Comment on his story of the blocks, boy, and mother.

A classification of systems

Depending on the modes of interaction between the systems and their surroundings, we classify systems into several types.

	transfer matter	transfer space	transfer energy
isolated system	no	no	no
thermal system	no	no	yes
closed system	no	yes	yes
open system	yes	yes	yes

Isolated system. An isolated system does not interact with its surroundings.

Thermal system. A *thermal system* interacts with its surroundings in one mode: transfer energy.

For example, a bottle of water is a thermal system. We cap the bottle to prevent molecules to leak in or out. We make the bottle rigid to fix its volume. We can still change the energy of the water by placing the bottle over a fire, or shaking the bottle, or electrical heating.

Closed system. A *closed system* and its surroundings do not transfer matter, but transfer space and energy.

Consider a cylinder-piston setup that encloses water molecules. Some water molecules form a liquid, and others form a vapor. We seal the piston, so that no molecules will leak in or out. The cylinder-piston setup interacts with the rest of the world in two ways. First, when weights are added on top of the piston, the piston moves down and reduces the volume inside the cylinder. Second, when the cylinder is brought over a fire, the fire heats up the water.

Open system. An *open system* and its surroundings transfer matter, space, and energy. A bottle of water, cap removed, is an open system.

Exercise. Describe a method to keep water hot for a long time. What can you do to prolong the time? What makes water eventually cool down?

Exercise. For each type of system listed above, give an example. In each example, describe all modes of interaction between the system and its surroundings.

Work and heat

A half bottle of water. Here is the half bottle of water again. I cap the bottle to prevent molecules from leaking in or out. I shake the bottle, or just touch it. In both cases, my hand transfers energy to the H_2O molecules in the bottle. In shaking the bottle, my hand transfers energy to the bottle by *work*, through force times displacement. In touching the bottle, my hand transfers energy to the H_2O molecules by *heat*, through the vibration of the molecules of my hand and the bottle.

The H_2O molecules in the bottle form a closed system. By definition, a closed system and its surroundings do not transfer matter, but transfer space and energy. Work and heat are two ways to transfer energy between the closed system and its surroundings.

A cylinder-piston setup. It is rather cumbersome to quantify the work due to the shake of my hand and the heat due to the touch of my hand. Let us use a more scientific experimental setup: a fluid, cylinder, pistorn, weight, and fire. The fluid in the cylinder consists of a fixed number of molecules. As the piston moves up, the volume V increases, and the fluid does work to the surroundings. The fire transfers energy by heat to the fluid. Thus, the fluid is a closed system, and the rest of the world is the surroundings. Let us see how we determine the work and heat.

Internal energy of a closed system

The internal energy of the fluid is a property, i.e., a function of state. A state of the fluid is specified by a pair of values of two independent properties, such as temperature T and volume V. Thus, the internal energy is a function of the two independent properties, U(T,V). We will soon describe how to measure this function experimentally.

Transfer energy by work

Work is a method to transfer energy between a system and its surroundings. We have learned many ways of doing work in mechanics and electrodynamics. Recall two examples.

The expansion of a fluid raises a weight. A piston seals a cylinder of fluid. On top of the piston, a block of mass and the pressure of the surrounding air apply a force F. Assume that the piston moves with no friction. The balance of the forces requires that $F = PA$, where P is the pressure of the fluid, and A is the base area. When the piston raises its height by dz, the fluid expands its volume by $dV = Adz$ and does work:

$dW = Fdz = PdV$.

This is the energy transfer by work from the fluid to the surroundings. The expansion of the fluid raises the weight.

Electrical work. As a second example, a resistor is placed in a container of water. When a voltage V is applied to the two ends of the resistor, an electric current I goes through the resistor, and the charge going through the resistor is $dq = Idt$, where dt is the increment of time. The work done by the voltage is

$dW = Vdq = VIdt$.

Transfer energy by heat

Definition of heat. Heat is a method to transfer energy between a system and its surroundings. For a closed system, heat is defined by

$Q = W + \Delta U$.

We do our best to identify various methods that transfer energy by work. Energy transfer by heat is then the transfer of energy that we do not bother to call work.

Internal energy is a thermodynamic property of the closed system. Neither transfer energy by work nor transfer energy by heat is a thermodynamic property of the closed system; they are methods of the transfer of energy between a closed system and its surroundings.

Transfer energy by heat in several ways

Conduction. Energy can go through a material. At a macroscopic scale, the material remains stationary. At a microscopic scale, energy is carried by the flow of electrons and vibration of atoms.

Convection. Energy can go from one system to another with the flow of a fluid. This way of energy transfer involves the transfer of matter between systems and is present for an open system.

Radiation. Energy can be carried by electromagnetic waves. Because electromagnetic waves can propagate in vacuum, two systems can transfer energy without being in proximity.

Sign convention

Given a closed system, we adopt the following sign convention.

- $Q > 0$, energy transfer by heat to the closed system from the surroundings.
- $W > 0$, energy transfer by work from the closed system to the surroundings.
- $\Delta U > 0$, increase of the internal energy of the closed system.

Some writers adopt other sign conventions. You can adopt any sign convention, so long as you make your sign convention explicit in the beginning of a thought, and do not change the sign convention in the middle of the thought.

Adiabatic process

A closed system is said to undergo an *adiabatic process* if the closed system is thermally insulated, so that no energy transfers by heat between the closed system and the surroundings, $Q = 0$.

The thermally-insulated, closed system and the surroundings can still transfer energy by work. By the definition of heat, write

$W + \Delta U = 0$.

In an adiabatic process, the change in internal energy of a closed system equals the negative of the work done by the closed system.

For example, a thermally-insulated, closed system can increase its internal energy through electrical work. We can fix the volume of the cylinder-piston setup, and applies the electrical work. In this way, we can measure the internal energy as a function of temperature and volume, $U(T, V)$.

Exercise. An 100-g apple, initial height 1 m, falls into a tank of water and comes to rest. Assume that tank is thermally insulated, what is the change in the internal energy of the combined water and apple?

Exercise. A cylinder-piston setup contains 1 kg of water and steam. The force acting on top of the cylinder is constant, subjecting the water and steam to a constant pressure of 200 kPa. The cylinder is placed over a fire, and changes volume from 0.1 m^3 to 0.5m^3. Determine the energy transfer by work and by heat. Sketch the process in a P-v diagram. Also include the water-steam dome in the diagram.

Constant-volume process

When the position of the piston is fixed, the volume of the cylinder is fixed, and the fluid does no work to the surroundings. In the constant-volume process, the closed system becomes a thermal system. When the fluid changes internal energy by dU, by definition, the fluid receives energy by heat:

$dQ = dU$.

In a constant-volume process, the heat received by the fluid equals the change in internal energy.

Constant-pressure process. Enthalpy

The volume of the fluid is $V = Az$, where A is the base area and z the height of the piston. The balance of forces acting on the piston requires that $F = PA$, where F is the force due to the weight of a block of mass, along with the weight of the air. The potential energy of the weight (i.e., the force F) is

$Fz = PAz = PV$.

Assume that the weight above the piston is fixed, so that the pressure P of the gas is fixed. The closed system undergoes a constant-pressure process. We now regard the fluid and the weight together as a composite system. The energy of the composite system is the sum of the internal energy of the fluid and potential energy of the weight: $U + PV$. The quantity

$H = U + PV$

is a property of the fluid, and is called *enthalpy*.

The composite has a fixed amount of matter, does not transfer energy by work to the surroundings, and receives energy by heat from the surroundings. Consequently, the composite is a thermal system.

By definition, the energy transfer between a thermal system and the surroundings is heat:

$dQ = d(U + PV)$.

In a constant-pressure process, the heat received by the fluid equals the change in enthalpy.

Thus, the fluid is a closed system. In a constant-pressure process, the composite of the fluid and the weight above the piston is a thermal system. The quantity $U + PV$ is the enthalpy of the closed system, the fluid, but is the energy of the thermal system, the composite.

We can also arrive at the above result as follows. When a closed system changes volume by dV, the closed system transfers energy to the surroundings by work:

$dW = PdV$.

By definition, when the closed system changes volume by dV and changes internal energy by dU, the closed system receives energy by heat:

$dQ = dU + PdV$.

In a constant-pressure process, the above equation becomes that

$dQ = d(U + PV)$.

Exercise. A closed system is said to undergo an adiabatic process if the system is thermally insulated. One kilogram of water at 500 Celsius and one kilogram of saturated steam, both at 200 kPa, are mixed in a constant-pressure and adiabatic process. Find the following quantities.

A. The final temperature.
B. The final volume.
C. The change in enthalpy for the process.
D. The change in internal energy for the process.
E. The change in entropy for the process.

Work and heat are superfluous ideas

Incorrect uses. The word “heat” permeates English, and is used as a verb, noun, and adjective. Consider a few uses in thermodynamics:

1. Heat a bottle of water by hand.
2. Electric heater.
3. Heat capacity.
4. Heat energy

Examples 1 and 2 are consistent with the definition in thermodynamics: the word “heat” just means a method of transfer energy. Examples 3 and 4 are inconsistent with the definition of the word “heat” in thermodynamics. Rather, I will use the phrases “thermal capacity” and “internal (or thermal) energy”.

As yet another example, the energy of phase change is commonly known by its historical name, *latent heat* (Black, 1750). This historical name is inconsistent with the definition of the word “heat” in thermodynamics. Energy of phase change is a difference in energy (a property), and should not be named using the word heat, a method of energy transfer. We can melt a block of ice by work, such as moving the block against friction.

If we keep track of the properties of both a system and its surroundings, heat and work are superfluous ideas. They merely relabel things that we already know: the systems and surroundings transfer energy, space, and matter. Thermodynamics is just as effective if we eliminate superfluous ideas like work and heat. Thus, if these two words confuse you in a sentence, eliminate them and rephrase the sentence in terms of energy, space, and matter.

I will restrict the use of heat and work to minimum, only when the two words shorten sentences and do not obscure ideas.

The word “heat” used in everyday life is usually unrelated to heat defined in thermodynamics. Outside thermodynamics, the word “heat” is used in many more ways. There is no reason to expect them to have anything to do with the definition of the heat in thermodynamics. Indeed, in popular usage, something “hot” is almost synonymous to something “cool”. English is a wonderful language, but is not invented for thermodynamics.

Exercise. Superfluous ideas lead to superfluous questions. Does electrical heater do work or transmit heat? An academic debate becomes hot when the stake is small.

The first law of thermodynamics

For historical reasons, the equation $Q = W + \Delta U$ is called the “first law of thermodynamics”. This phrase abuses the word “law”. The equation is not a law; it just defines the word “heat” as a method to transfer energy.

The definition of heat vs. the principle of the conservation of energy. Many textbooks claim that the equation $Q = W + \Delta U$ is a statement of the principle of the conservation of energy. This claim is incorrect. The principle of the conservation of energy is much broader than the definition of heat as a method to transfer energy.

In applying the principle of the conservation of energy, we need to know how energy relates to other variables. For example, the potential energy is the weight times height, the kinetic energy is half the mass times the velocity squared, and the electrical energy is the voltage times charge. These relations are determined in various sciences, outside thermodynamics.

Equating the principle of the conservation of energy and the first law of thermodynamics is unfair and misleading. The equation $Q = W + \Delta U$ is too limited to reach the scope of the principle of the conservation of energy. We must spend time to learn how various forms of energy behave, far beyond the narrow concern of the definition of heat.

I will separate the two distinct matters: the definition of heat and the conservation of energy. To focus on matters of substance, I will drop the term “the first law of thermodynamics”, and use the term “the principle of the conservation of energy”.

Thermal energy of ideal gas

Thermal capacity of ideal gas

A fixed amount of an ideal gas is a closed system, characterized by two equations:

$PV = Nk_BT$,
$dU = Nc_V(T)dT$.

We have studied the first equation. For now we regard both equations as empirical facts.

We can specify a state of the gas by a pair of values of temperature and volume, (T, V). For a general closed system, the pressure is a function of temperature and volume, P(T,V). For an ideal gas, this function takes the form of the ideal gas law, $P = NkT/V$.

For a general closed system, the internal energy is also a function of temperature and volume, U(T,V). For an ideal gas, the internal energy is a function of temperature, and is independent of volume. The function $c_V(T)$ is the *thermal capacity* per molecule.

The second equation failed to obey the rule: whenever temperature is reported in Kelvin, temperature should appear as k_BT. This disobedience has a consequence: now the thermal capacity has the fake unit J/K. One lie leads to another; to lie consistently is hard.

Thermal capacity per mole or per unit mass is also commonly used. Thermal capacity of an ideal gas is a function of temperature. The function has been determined for many species of molecules, and is available online and at the back of textbooks.

Exercise. In a helium gas, each molecule consists of a single helium atom. For such a gas of single-atom molecules, the thermal capacity per molecule is $c_V = 1.5k_B$, and is independent of temperature. Calculate the thermal capacity per mole of helium. Calculate the thermal capacity per unit mass of helium. The molar mass of helium is 4 g/mole.

Energy transfer by work and by heat

When the volume of the gas changes by dV, the energy transfer by work from the gas to the surroundings is

$dW = PdV$.

When the volume of the gas changes by dV and the internal energy of the gas change by dU, the energy transfer by heat from the surroundings to the gas is

$dQ = dU + PdV$.

Neither the energy transfer by work nor the energy transfer by heat is a function of state; they depend on process. We next consider several processes.

Constant-volume process

Subject to a constant volume, the gas does no work: W = 0. Consequently, the energy transfer by heat equals the change in internal energy:

$dQ = Nc_V(T)dT$.

When the temperature changes from T_1 to T_2, assuming the thermal capacity is independent of temperature, the energy transfer by heat is

$Q = Nc_V(T_2 - T_1)$.

If the thermal capacity is a function of temperature, we calculate the energy transfer by heat by integration.

Constant-pressure process

Consider the experimental setup of a gas, cylinder, pistorn, and weight. Assume that the weight placed above the piston is fixed, so that the pressure of the gas is fixed.

When the volume changes by dV, the gas does work $dW = PdV$. When the volume changes from V_1 to V_2 under a constant pressure P, the gas goes work

$W = P(V_2 - V_1)$.

In general, the energy transfer by heat both changes the internal energy and volume: $dQ = dU + PdV$. Subject to a constant pressure, this expression becomes that

$dQ = d(U + PV)$.

Recall that the quantity $U + PV$ is the enthalpy. Thus, in a constant-pressure process, the transfer of energy by heat equals the change in enthalpy.

For an ideal gas under a constant pressure, the energy transfer by heat is

$dQ = N(c_V(T) + k_B)dT$.

The quantity $c_V(T) + k_B$ is the thermal capacity per molecule under constant pressure, and is designated as $c_P(T)$:

$c_P(T) = c_V(T) + k_B$.

Isothermal process

A constant-temperature process is also called an *isothermal process*. Because of the ideal gas law, the isothermal process is characterized by a curve PV = constant. Recall the definition of heat, $dQ = dU + dW$. For an ideal gas, the isothermal process does not change the internal energy, so that the energy transfer by heat to the closed system is the same as the work done by the closed system:

$dW = dQ = (NkT/V)dV$.

When the volume changes from V_1 to V_2, the energy transfer by heat is

$W = Q = Nk_BT \log (V_2/V_1)$.

Adiabatic process

In an adiabatic process, no energy transfers by heat between the closed system and the surroundings:

$Q = 0$.

Thus,

$dU + PdV = 0$.

For an ideal gas, this equation becomes

$c_V(T)dT + (k_BT/V)dV = 0$.

We further assume that the thermal capacity is independent of temperature. Integration yields

$c_V \log T + k_B \log V$ = constant,

or

TV^{k-1} = constant,

where $k = c_P/c_V$. The constant is determined by one state in the process, say the initial state (T_i,V_i). Thus, constant = $T_iV_i^{k-1}$.

Caution. The result TV^{k-1} = constant explains *adiabatic cooling* when a gas expands in an adiabatic process, and explains *adiabatic heating* when a gas contracts in an adiabatic process. The phrase "adiabatic heating" is inconsistent with the definition of the word "heat" in thermodynamics. In an adiabatic process, a closed system is thermally insulated, and does not transfer energy by heat. When the volume contracts, the external force does work to the closed system, so that the internal energy increases. The word "heating" in the phrase "adiabatic heating" means increasing internal energy by work.

Recall the ideal gas law $PV = Nk_BT$. The adiabatic process also obeys that

PV^k = constant.

When the volume changes by dV, the adiabatic process transfers energy by work:

$dW = PdV$ = (constant) $V^{-k}dV$.

Integration yields

W = (constant/(k - 1)) $(V_1^{-k+1} - V_2^{-k+1})$

Exercise. Assume that an ideal gas has a constant thermal capacity per molecule c_V. One mole of the ideal gas changes from an initial state (P_i,V_i) to a final state (P_f,V_f) along a straight line on the (P,V) plane. Calculate the energy transfer by work and energy transfer by heat. Calculate the changes in internal energy.

Exercise. An ideal gas undergoes an adiabatic process from an initial state (P_i,V_i) to a final state of volume V_f. Calculate the pressure of the final state, P_f. Calculate the energy transfer by work in the adiabatic process.

Basic algorithm of thermodynamics

Fundamental postulate

Enough about the fake unit, unnecessary reference, and superfluous ideas. Let us return to the stage of the play—the world. Let us cast light on the leading role—entropy.

Facts. Of our world we know the following facts:

1. An isolated system has a certain number of quantum states. Denote this number by Ω.
2. The isolated system flips from one quantum state to another, rapidly and ceaselessly.
3. A system isolated for a long time flips to every one of its quantum states with equal probability, 1/Ω .

Thus, a system isolated for a long time behaves like a *fair die*:

1. The die has six faces.
2. The die is rolled from one face to another.
3. The die is rolled to every face with equal probability, 1/6.

Fact 3 of the world is called the *fundamental postulate*. The fundamental postulate cannot be deduced from more elementary facts, but its predictions have been confirmed, without exception, by empirical observations. We will regard the fundamental postulate as an empirical fact, and use the fact to build thermodynamics.

The fundamental postulate links thermodynamics and probability. Nature acts like a maniac gambler, ceaselessly and rapidly throwing numerous fair dies, each die having numerous faces.

	Probability	Thermodynamics
Experiment	Roll a fair die	Isolate a system for a long time
Sample space	6 faces	Ω quantum states
Probability of a sample point	1/6	1/Ω
Subset of sample space	Event	Subset, thermodynamic state

Probability to realize a subset	(number of faces in the subset)/6	(number of quantum states in the subset)/Ω
A function from sample space to a set of values	Random variable	Internal variable, thermodynamic property

Exercise. A cheater makes an unfair die of six faces, labeled a,b,c,d,e,f. Through many throws, the cheater finds that the probability of face a is ½, the probability of face f is 1/10, and the other four faces have an equal probability. What is the probability of getting face b twice in two throws?

Random variable

We will not need detailed techniques in probability, but will need a concept—random variable. As we will see, in thermodynamics, a random variable is called an internal variable.

Let A be the sample space of an experiment, and X be a set. A random variable F is a function that maps the sample space A to the set X. Write

F: A→X.

When a trial of the experiment produces a sample point a ∈ A, the function F takes the value x ∈ X. Write

F(a) = x.

A function F is specified by three sets: domain, range, and map. The domain is the sample space A, which consists of all the sample points of the experiment. The range is the set X, which consists of any objects we care about. The map is the set of all ordered pairs of the form (a, x), where a is each sample point in A, and x is the corresponding object in X.

The function F is deterministic, but the outcome of a trial of the experiment is random. Consequently, each trial of the experiment produces a random value in X.

Example. Consider a die with faces labeled as {a,b,c,d,e,f}, which constitutes the sample space of the experiment, a roll of the die. Before rolling the die, we agree on a rule of winning: $2 for face a, $6 for face b, $1 for face c, $4 for face d, $0 for face e, $2 for face f. This rule of winning is a random variable, a function that sends each face of the die to an amount of winning. The domain of the function is the sample space—the set of the six faces, {a,b,c,d,e,f}. The range of the function is a set of numbers—the set of amounts of winning {$0, $1, $2, $4, $6}. Whereas the rule of winning is deterministic, the face obtained from each roll of the die is random, and the amount of winning after each roll of the die is random.

Exercise. We agree on the above rule of winning. What is the probability of winning $7 after rolling a fair die three times?

Ignorance is bliss

In throwing a die, the gambler does not need to know the material that makes the die. The die can be made of wood, plastic, or metal. Nor does the gambler care how each face is marked. The faces can be marked by numbers, dots, or any other symbols. All the gambler needs to know is that the die has six distinct faces of equal probability.

The same is true in thermodynamics. We do not need to know the quantum states themselves (the shape of the cloud of electrons, the positions of nuclei, or the number of protons). We just need to know how many distinct quantum states that an isolated system has.

This enormous reduction of information is central to the success—and the limitation—of thermodynamics. An isolated system is reduced to a pure number, the number of quantum states, Ω. Thermodynamics teaches us how to count, curate, and use the numbers of quantum states of isolated systems.

Let us watch the fundamental postulate act.

Dispersion of ink

Fact. Drip a drop of ink into a bottle of water, and the ink disperses over time.

Experiment 1. The dispersion of ink is readily observed at macroscopic scale. YouTube dispersion of ink.

Experiment 2. The ink contains pigment particles of size less than a micron. The motion of individual pigment participles can be observed in a microscope. YouTube Brownian motion.

Interpretation. Each pigment particle is bombarded by water molecules, rapidly and ceaselessly, from all directions. The pigment particle is much larger than an individual water molecule. At any given time, the bombardments do not fully cancel out, but result in a net force, which moves the pigment particle. This rapid, ceaseless, random motion of a particle in water was first observed in a microscope by Robert Brown (1827). Wiki Brownian motion.

Question. Individual pigment particles move in all directions *randomly*. After some time, the pigment particles disperse in the bottle of water *homogeneously*. How can the random motion of individual pigment particles cause them collectively to do something directional—dispersion?

Theory. When the concentration of pigment particles is inhomogeneous, more particles will diffuse from a region of high concentration to a region of low concentration. This bias continues until the pigment particles distribute in water homogeneously.

Let us relate this everyday experience to the fundamental postulate. To make a definite calculation, we assume that individual pigment particles are far apart, so that each particle is free to explore everywhere in the bottle of water, unaffected by the presence of other pigment particles. Consequently, the number of quantum states of each pigment particle is proportional to the volume of the water in the bottle, V. The number of quantum states of N pigment particles is proportional to V^N.

On the other hand, if the N pigment particles are localized in a small region, say, in the initial drop of ink of volume V/70, the number of quantum states of the N pigment particles is proportional to $(V/70)^N$.

After the ink is in water for a long time, all quantum states are equally probable. Thus, the ratio of the probability of finding the N pigment particles in volume V to the probability of finding the N pigment particles in volume V/70 is 70^N. This ratio is enormous because a drop of ink has a large number of pigment particles, N. This fact explains why the pigment particles much, much prefer dispersion to localization.

Exercise. The density of the pigment material is 1000 kg/m^3. Assume each pigment particle is a sphere, diameter 100 nm. How many pigment particles are there in 1g of dry ink? After the ink is in a bottle of water, volume 100 ml, for a long time, what is the ratio of the probability of finding all pigment particles in a volume of 10 ml to the probability of finding all pigments in the volume of 100 ml?

Separation of phases

Fact. A half bottle of water isolated for a long time equilibrates in two phases: liquid and gas.

I shake the bottle. Water sloshes and bubbles pop. I stop shaking, and the half bottle of water becomes approximately an isolated system. Right after the isolation, the half bottle of water is still out of equilibrium. After being isolated for some time, the half bottle of water calms down at macroscopic scale. In equilibrium, some water molecules form liquid, and others form gas.

Theory. We are not ready to develop a full theory of liquid-gas phase separation. We begin with a few ideas here, and pick them up later. We idealize the H_2O molecules in the bottle as an isolated system. The isolated system flips among a set of quantum states. Denote the number of quantum states of the isolated system by Ω.

Let M be the total number of H_2O molecules in the bottle. The number of H_2O molecules in the gas, N, can take one of a set of values:

{0,1,...,M}.

When the number of H_2O molecules in the gas is fixed at N, the isolated system flips among quantum states in a *subset of the sample space*. Denote the number of quantum states in this subset by Ω(N). Thus,

Ω(0) + Ω(1) + … + Ω(M) = Ω.

Probability. After the bottle is isolated for a long time, every quantum state in the sample space is equally probable, so that the probability to observe N molecules in the gas is

Ω(N)/Ω.

In equilibrium, the most probable number of molecules in the vapor, N, maximizes the function Ω(N).

From probability to (almost) certainty. The half bottle of water is a macroscopic isolated system, and has a sample space of a large number of quantum states. In equilibrium, the fluctuation in the number of molecules in the gas is exceedingly small compared to the mean, and the observed number of molecules in the vapor is well described by the number N that maximizes the function Ω(N). The function Ω(N) has a sharp peak.

Exercise. A 1-liter bottle is half-filled with water. The bottle is capped, and the temperature is fixed at 25 Celsius. Use the steam table and ideal gas law to determine the number of H_2O molecules in the gas inside the bottle.

Subsystems

The two phenomena—dispersion of ink and separation of phases—illustrate characteristics common to all isolated systems. We next describe these common characteristics in turn.

It makes no sense to talk about equilibrium at the level of a few pigment particles. Equilibrium will prevail in a large number of pigment particles.

When an isolated system is in equilibrium, any part of the isolated system is also in equilibrium, so long as the part is macroscopic.

We can divide the isolated system into many parts. Each part is large compared to individual particles, but small compared to the entire isolated system. We regard each part as a *subsystem*, which is also an isolated system. The subsystem, regarded as an isolated system, has its own sample space of quantum states. Thus, the entropy of an isolated system is the sum of the entropies of all parts of the system.

In the dispersion of ink, we can divide the whole body of water into many parts, each part being much larger than individual pigment particles.

In the separation of phases, we can divide the half bottle of water into two subsystems: liquid and gas.

Constraint internal to an isolated system

When an isolated system is out of equilibrium, we often divide the isolated system into parts. For example, before the ink is fully dispersed in the bottle of water, we may divide the bottle into many small volumes. Each small volume has a large number of pigment particles, which are approximately homogeneously distributed, so that we can think of each small volume as an isolated system, with its own sample space of quantum states. The isolated system is said to be in *constrained equilibrium.*

Fixing the number of water molecules in the gas in the half bottle of water is an example of a *constraint internal to an isolated system*. The constraint can be made literal by placing a seal between the liquid and vapor. With the seal, the two parts of the isolated system can separately reach equilibrium, but are not in equilibrium with each other. The isolated system is in constrained equilibrium.

Internal variable

When the constraint internal to the isolated system is removed, the number of H_2O molecules in the vapor, N, can change. The number N is called an *internal variable*.

In dispersion of ink, the internal variable is the volume in which all the pigment particles are located.

Let us abstract the two examples to formalize the concept of internal variable in general terms.

Sample space. An isolated system has a set of quantum states, which constitute the sample space. Denote the total number of quantum states of the isolated system by Ω.

Internal variable. Let X be a set of values:

$X = \{x_1,..., x_n\}$.

An internal variable is a function that maps the sample space to the set X. In probability, such a function is called a *random variable*.

Subset of sample space. When a constraint internal to the isolated system fixes the internal variable at a value x in the set X, the isolated system flips among quantum states in a *subset of the sample space*. Denote the number of quantum states in this subset by $\Omega(x)$.

The internal variable dissects the sample space into a family of subsets. Any two subsets in the family are disjoint. The union of all the subsets in the family is the sample space. Thus,

$\Omega(x_1) + \ldots + \Omega(x_n) = \Omega$.

Probability. After the constraint is removed for a long time, the isolated system flips to every one of its Ω quantum states with equal probability, and the internal variable can take any value in the set X. In equilibrium, the probability for the internal variable to take a particular value x in the set X is

$\Omega(x)/\Omega$.

From probability to (almost) certainty. The function $\Omega(x)$ has a sharp peak. After the constraint is removed for a long time, the observed value of the internal variable is well described by the value x that maximizes the function $\Omega(x)$.

Exercise. In the dispersion of ink, identify the isolated system and internal variable.

Exercise. In the separation of phases, identify the isolated system and internal variable.

Equilibrium

Fact. A system isolated for a long time reaches *equilibrium*.

We have watched the evolution to equilibrium in concrete examples.

- A bottle of air equilibrates in a homogenous mixture of several species of molecules.
- A half bottle of water equilibrates in a state of two phases: water and steam.
- A half bottle of water equilibrates in a state of there phases: water, ice, and steam.

We have also watched ink disperse. Right after a small drop of ink enters the bottle of water, all the pigment particles are localized in the drop. The pigment particles then start to diffuse into the pure water. After some time, the pigment particles disperse in the bottle of water homogeneously. The system of the pigment particles in water is said to have reached equilibrium.

Theory. In or out of equilibrium, an isolated system flips from one quantum state to another, ceaselessly and rapidly.

Right after isolation, the system has Ω quantum states, flips to some of them more often than others, and is said to be out of equilibrium. Out of equilibrium, the probability for the isolated system to be in a quantum state is time-dependent.

After being isolated for a long time, the system flips to every one of its quantum states with equal probability, 1/Ω, and is said to have reached equilibrium. In equilibrium, the probability for the isolated system to be in a quantum state is time-independent.

A macroscopic isolated system has a sample space of a large number of quantum states. Associated with a constrain internal to the isolated system is an internal variable. When the internal variable is fixed at a value x, the isolated system flips among the quantum states in a subset of the sample space. Denote the number of quantum states in this subset by Ω(x). The function Ω(x) has a sharp peak. After the constraint is removed for a long time, the observed value of the internal variable is well described by the value x that maximizes the function Ω(x).

Several phrases are synonymous. A system "isolated for a long time" is a system "flipping to every one of its quantum states with equal probability", and is a system "in equilibrium". Whenever we speak of equilibrium, we identify a system isolated for a long time.

Caution. In or out of equilibrium, an isolated system has a fixed sample space of Ω quantum states. The entropy of an isolated system, S = log Ω, is a fixed number and does not change, no matter whether the isolated system is in or out of equilibrium.

Reversibility

Fact. An isolated system can undergo reversible change. A frictionless pendulum swings forever.
A falling apple loses height, but gains velocity. So long as the friction between the apple and the air is negligible, the sum of the potential energy and kinetic energy of the apple is constant.

Theory. We model the apple, together with a part of space around the apple, as an isolated system. The height of the apple is the internal variable of the isolated system. When the apple is at a particular height, z, the isolated system flips among a set of quantum states, and has a certain entropy, S(z). The process of falling keeps the subset entropy S(z) fixed, independent of the internal variable z. Such a process is called an *isentropic process*.

An isentropic process of an isolated system is *reversible*. We can arrange a setup to return the apple to its original height without causing any change to the rest of the world. For example, we can let the apple fall along a curved slide. So long as friction is negligible, the apple will return to the same height.

Of course, friction is inevitable in reality; we have never seen an apple go up and down a slide for a long time. The apple inevitably stops after some time. But a frictionless process can be a useful idealization. For example, the planet Earth has been moving around the Sun for a very long time.

The two words, *isentropic* and *reversible,* are equivalent. Both adjectives describe an isolated system that keeps the number of quantum states unchanged when an internal variable changes. An isentropic (i.e., reversible) process is also called a *quasi-equilibrium process*. To avoid increasing the subset entropy, the process must be slow enough for the isolated system to have a long enough time to reach equilibrium at every point along the process.

The entropy in the word “isentropic” means the subset entropy—the entropy of the subset of the sample space as a function of the internal variable, $S(z)$. The total entropy of an isolated system is always constant, in or out of equilibrium.

Exercise. Describe another isentropic process.

Irreversibility

Fact. Once in equilibrium, the isolated system will *not* go out of equilibrium.

The isolated system out of equilibrium is said to approach equilibrium with *irreversibility*.

Theory. So long as the bottle is isolated, the homogeneously dispersed pigment particles will be extremely unlikely to come back into a small volume. We have just seen the enormous difference in probability between dispersion and localization.

Right after being isolated, the system is out of equilibrium. As time moves forward, the isolated system evolves toward equilibrium, and the internal variable changes in a sequence of values that increase the function $\Omega(x)$. So long as the system is isolated, the change in the internal variable is irreversible.

Arrow of time. Thermodynamics uses the *direction of time*, but not the *duration of time*. Thermodynamics makes no use of any quantity with dimension of time. Time enters thermodynamics merely to distinguish between “before” and “after”. Irreversibility gives time the direction, the *arrow of time*.

Fluctuation

In equilibrium, the pigment particles keep in ceaseless Brownian motion. The distribution of the pigment particles *fluctuates*. Possibly all pigment particles can move into a small volume in the bottle. However, the probability of finding a nonuniform distribution is exceedingly small. This course will ignore fluctuation.

Kinetics

A system isolated for a long time flips to every one of its quantum states with equal probability. How long is long enough? The fundamental postulate is silent on this question. The pigment particles disperse slower in cold water than in hot water. The time needed to reach equilibrium scales with the viscosity of the liquid. The study of how fast a system evolves is called *kinetics*, which does not belong to thermodynamics.

Basic algorithm of thermodynamics (BAT)

Internal variable x is a function that maps the sample space A of an isolated system to a set X.

Function Ω(x). When the internal variable takes a value x in the set X, the isolated system flips among the quantum states in a subset of the sample space. Denote the number of quantum states in the subset by Ω(x).

After a system is isolated for a long time, and after the internal variable is fixed at the value x for a long time, the isolated system flips to every quantum states in the subset with equal probability.

Function S(x). Define S(x) = log Ω(x). Because logarithm is an increasing function, increasing Ω(x) is equivalent to increasing S(x).

The function S(x) stands for “the logarithm of the number of quantum states in the subset of the sample space of an isolated system when an internal variable is fixed at x”. The function S(x) is fundamental to thermodynamics, but is unnamed. For brevity, I will call the function S(x) the *subset entropy*.

Basic algorithm of thermodynamics (BAT). The algorithm has four steps:

1. Construct an isolated system with an internal variable x.
2. Find the subset entropy of the isolated system as a function of the internal variable, S(x).
3. *Equilibrium*. Find the value of the internal variable x that maximizes the function S(x).
4. *Irreversibility*. Change the value of the internal variable x in a sequence that increases the function S(x).

To maximize something, we need a function. To specify a function, we need both a dependent variable, and one or many independent variables. The dependent variable is the entropy of the subset (i.e., the logarithm of the number of quantum states in the subset of the sample space of an isolated system). The independent variable is the internal variable, which specifies the subset.

In applications, an isolated system may have multiple internal variables. The BAT applies just the same. We will see numerous examples of applying the BAT as we go along.

Exercise. Use the basic algorithm to analyze the dispersion of ink. Identify the four steps.

Khan Academy Maxwell's demon

The second law of thermodynamics

The basic algorithm is one of many alternative statements of *the law of the generation of entropy*, or *the second law of thermodynamics*. Not all statements of the second law are equivalent. Many are misleading and even wrong.

We will list some historical statements of the second law of thermodynamics. They may sound like ancient philosophical pronouncements. They sound mysterious not because they are more profound than BAT, but because they miss facts of nature (e.g., the rapid and ceaseless flips among quantum states, the fundamental postulate, and the internal variables).

Here is one such statement made by Clausius (1865), in the same paper in which he coined the word entropy:

The entropy of the universe tends to a maximum.

We will take the word *universe* to mean an isolated system. This statement is adopted by numerous textbooks. The statement is elegant but wrong, if taken literally. The entropy of an isolated system is $S = \log \Omega$, where Ω is the total number of quantum states in the entire sample space of the isolated system. The entropy of an isolated system is a fixed number, not a function that can change value and be maximized.

To talk about a macroscopic change of an isolated system, we need to identify an internal variable. When a constraint internal to the isolated system fixes the internal variable at a value x, the isolated system flips among quantum states in a subset of the sample space. The number of quantum states in this subset is $\Omega(x)$, and the entropy of this subset is $S(x) = \log \Omega(x)$. When the constraint internal to the isolated system is removed, the internal variable x can change values. It is the subset entropy $S(x)$ that tends to a maximum.

When elegance and clarity conflict, we go for clarity.

This book does not teach the history of thermodynamics. We do not attempt to read the mind of Clausius and decipher old pronouncements. Rather, we will use the basic algorithm to direct calculation and measurement. In particular, the basic algorithm will let us count, experimentally, the number of quantum states in the subset of the sample space when the internal variable of the isolated system is fixed, Ω(x).

Thermal system

Entropy and energy

Now that you have seen both entropy and energy, you are ready to critique the following extract from a founding paper of thermodynamics (Clausius 1865).

We might call S the transformational content of the body, just as we termed the magnitude U its thermal and ergonal content. But as I hold it to be better to borrow terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call the magnitude S the *entropy* of the body, from the Greek word *τροπη*), transformation. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.

1. The energy of the universe is constant.
2. The entropy of the universe tends to a maximum.

Google Books. Rudolf Clausius, The Mechanical Theory of Heat, 1867. This book collects papers by Clausius on thermodynamics.

Exercise. Critique this extract. Take the word “universe” to mean, as many modern textbooks do, “an isolated system”. Do you agree that entropy and energy are nearly allied in their physical meanings? How can the entropy of an isolated system increase?

A family of isolated systems of a single independent property

Thermodynamics will use these conserved quantities as internal variables. Of course, internal variables need not be restricted to conserved quantities. This said, all conserved quantities obey similar arithmetics, and are convenient to study in parallel.

We have met an all-star cast of actors. Let us watch them play, act by act.

Act one: **The union of entropy and energy produces a child—temperature**. The child, temperature, is so prodigious that it is better known than its parents—entropy and energy. Let us watch entropy and energy (1) unite and (2) produce temperature.

Characteristic function S(U) of a thermal system. A thermal system and its surroundings interact in only one mode: transfer energy. The energy of the thermal system is in the form of thermal energy (internal energy)—that is, kinetic energy and potential energy at the scale of molecules. We can change the energy of the system by placing it over a fire, by shaking it, or by using an electric heater. As we have learned in daily life, chemical, mechanical, and electrical energy readily converts to thermal energy.

When the energy of the thermal system is fixed at a value U, the thermal system becomes an isolated system. Denote the number of quantum states of this isolated system by Ω(U).

As the energy U of the thermal system varies, the function Ω(U), or its equivalent, S(U) = log Ω(U), characterizes the thermal system as *a family of isolated systems*. The family has a single *independent property*, the thermal energy U. Each member isolated system has a specific value of thermal energy, U, flips among its own sample space of quantum states, and has its own number of quantum states, Ω(U).

A thermal system unites entropy and energy. We call S(U) the *characteristic function* of the thermal system. Later we will determine this function by experiment—that is, we will count the number of quantum states of each member isolated system experimentally.

Hydrogen atom. A hydrogen atom changes its energy by absorbing photons. When isolated at a particular value of energy, the hydrogen atom has a fixed set of quantum states. Each quantum state in the set is characterized by a distinct electron cloud and spin.

The hydrogen atom is a thermal system. Its characteristic function has been computed in quantum mechanics:

$\Omega(-13.6\text{eV}) = 2$,
$\Omega(-3.39\text{eV}) = 8$,
$\Omega(-1.51\text{eV}) = 18$,
……

The domain of the function Ω(U) is a set of discrete values of energy: −13.6eV, -3.39eV, -1.51eV ,… The range of the function Ω(U) is a set of integers: 2, 8, 18,…. For the hydrogen atom, the values of energy have large gaps.

A half bottle of water. We fix the amount of matter by sealing the bottle. We fix the space by making the bottle rigid. We transfer energy to the H_2O molecules inside the bottle. We do so in many ways—touch, fire, shake, and electric current, etc.

The half bottle of water is a thermal system. For such a complex thermal system, the values of energy are so closely spaced that we regard the energy of the system as a continuous real variable. The characteristic function of the thermal system, S(U), is a continuous function.

Exercise. Describe a few more examples of thermal systems.

Energy-entropy plane

Energy is a scalar set. Energy is an extensive property. The addition of two values of energy gives another value of energy. A value of energy times a real number gives another value of energy. Using words in linear algebra, we call energy U a *scalar*. All values of energy form a *scalar set*. A scalar set is just a *one-dimensional vector space*.

Entropy is a scalar set. Entropy is also an extensive property. We can add two values of entropy, and multiply a value of entropy by a real number. All values of entropy form a scalar set.

Energy and entropy form a two-dimensional vector space. A pair of the values of energy and entropy (U,S) is a *vector*. All pairs of energy and entropy form a *two-dimensional vector space.* We add energy to energy, and add entropy to entropy. But we never add energy to entropy. We multiply energy and number, and multiply entropy and number. But we do not multiply energy and energy, or entropy and entropy, or energy and entropy.

Picture a two-dimensional vector space. In a plane, we draw energy as the horizontal axis, and entropy as the vertical axis. We call this plane the energy-entropy plane. A point in the plane represents a pair of values of energy and entropy. All points in the plane represent the two-dimensional vector space.

Drawing the two axes perpendicularly in a plane is a convention. What does it even mean that energy is perpendicular to entropy? The statement has no experimental significance. Nature works well if we draw the two axes with an arbitrary angle, or do not draw them at all. But we will follow the convention and draw the two axes perpendicularly in the plane.

In the words of linear algebra, the energy-entropy plane is a two-dimensional vector space without inner product.

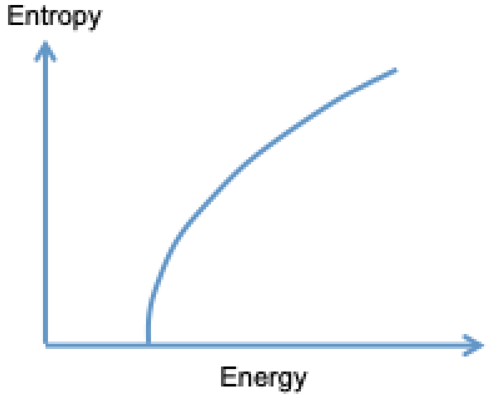
Features of the function S(U) common to all thermal systems

We characterize a thermal system with a function S(U), which is a *curve* in the energy-entropy plane.

The form of the function S(U) is specific to individual thermal systems, but several features are common to all thermal systems. We list here these common features in mathematical terms of the curve S(U), and will relate them to experimental observations as we progress.

1. Because energy is relative, the curve S(U) can translate horizontally without affecting the behavior of the thermal system.
2. Because entropy is absolute, the curve starts at S = 0, and cannot be translated up and down.

3. The behavior of a thermal system is often independent of the size of the system. For example, 1 kg of water and 2 kg of water freeze at the same temperature, zero Celsius. Both energy and entropy are extensive properties, linear in the size of the thermal system. As we change the size of the thermal system, the curve S(U) changes size, but keeps the shape.
4. The more energy, the more quantum states. Thus, Ω(U) is an increasing function. Because logarithm is an increasing function, S(U), is also an increasing function. That is, the slope of the curve S(U) is positive, $dS(U)/dU > 0$. As we will see, the slope of the curve S(U) defines temperature T: $1/T = dS(U)/dU$. Temperature is a child of energy and entropy: temperature is a derivative of energy and entropy.
5. As entropy approaches zero, the curve S(U) approaches the horizontal axis vertically. That is, as $S \to 0$, $dS(U)/dU \to \infty$.
6. The curve S(U) is *convex upward*. That is, the slope dS(U)/dU decreases as U increases, or equivalently, $d^2S(U)/dU^2 < 0$. We will define thermal capacity C by $1/C = dT(U)/dU$. Thermal capacity is a grandchild of energy and entropy. (There are significant exceptions to this feature. Later we will examine thermal systems of which the curve S(U) is *not* convex upward.)



Exercise. We have defined temperature T by $1/T = dS(U)/dU$, and defined thermal capacity C by $1/C = dT(U)/dU$. We will soon describe experimental observations that motivate these definitions. But here please derive an identity:

$1/C = -(d^2S(U)/dU^2)/(dS(U)/dU)^2$.

Thermodynamics is full of such identities. Most of them are useless and ignored.

Phrases associated with a family of isolated systems

A single isolated system. For a single isolated system, as noted before, several phrases are synonymous: a system “isolated for a long time” is a system “flipping to every one of its quantum states with equal probability”, and is a system “in equilibrium”.

Whenever we speak of equilibrium, we identify a system isolated for a long time. Associated with each isolated system is a set of quantum states, which constitute the sample space of the isolated system. The isolated system flips to its quantum states ceaselessly and rapidly. Out of equilibrium, the isolated system flips to some of its quantum states more often than others. In equilibrium, the isolated system flips to every one of its quantum states with equal probability.

In or out of equilibrium, an isolated system has a fixed sample space, a fixed number of quantum states, Ω, and a fixed entropy, $S = \log \Omega$.

A family of isolated systems. A thermal system is a family of isolated systems, specified by a single independent property—energy. Each member in this family is a particular isolated system, has a fixed value of energy, and flips among the quantum states in the sample space of the particular isolated system.

We describe a family of isolated systems using several additional phrases. These phrases are applicable to any family of isolated systems, and we have used them liberally before. Here we make these phrases precise for a family of isolated systems that constitute a thermal system.

Thermodynamic state. In a family of isolated systems, a member isolated system, once being isolated for a long time, reaches equilibrium. A member isolated system in equilibrium is called a *thermodynamic state*.

We now use the word “state” in two ways. An isolated system has many quantum states, but a single thermodynamic state. A thermodynamic state is synonymous to an isolated system in equilibrium. In a thermodynamic state, the isolated system flips to every one of its quantum states with equal probability. A quantum state is a sample point in the sample space of an isolated system. A thermodynamic state is an isolated system in equilibrium, a member of a family of isolated systems.

A thermal system is a family of isolated systems. Each member isolated system corresponds to one thermodynamic state of the thermal system, specified by a value of energy. As energy varies, the thermal system can be in many thermodynamic states.

Thermodynamic process. A sequence of thermodynamic states is called a *reversible thermodynamic process*, or a *quasi-equilibrium process*. Each thermodynamic state in this process corresponds to a distinct isolated system in equilibrium. A thermodynamic process is synonymous to a family of isolated systems, each being in equilibrium.

A thermal system can undergo only one type of thermodynamic process: changing energy. After each change of energy, we isolate the thermal system long enough to reach equilibrium.

On the energy axis, each point corresponds to a thermodynamic state, and each segment corresponds to a thermodynamic process.

Function of state. We specify a thermodynamic state of the thermal system by a value of energy. Energy is called a *function of state*. The word *state* here means thermodynamic state, not quantum state. A function of state is also called a *thermodynamic property*.

A thermal system is a family of isolated systems of a single variable. Once the energy of the thermal system is fixed, the member isolated system is fixed, and a thermodynamic state is also fixed.

Entropy is also a function of state. We can also specify a thermodynamic state of a thermal system by a value of entropy, a point on the entropy axis. For a thermal system, we will soon introduce other functions of state, such as temperature, thermal capacity, Massieu function, and Helmholtz function.

Equation of state. Once the energy U is fixed, a thermal system becomes an isolated system of a fixed sample space, so that the entropy S is also fixed. Consequently, given a thermal system, the energy and entropy are related. The relation S(U) is called an *equation of state*. Again, the word *state* here means thermodynamic state, not quantum state.

In general, an equation of state is an equation that relates the thermodynamic properties of a family of isolated systems. For a thermal system, we will soon introduce several equations of state, in addition to S(U).

Dissipation of energy

Facts. When I shake a half bottle of water, the energy in the muscles of my hand transfers to the H_2O molecules in the bottle.

I can also transfer energy to the H_2O molecules in the bottle using an electric current. This transfer of energy goes through several steps. An electric outlet transfers energy by work to a metal wire, where the voltage of the electric outlet moves electrons in the metal wire. The resistance of the metal wire heats up the metal wire. The metal wire is immersed in the water, and transfers energy by heat to the water.

I can also drop a weight into the bottle of water from some height. The weight comes to rest in the water.

In the three examples, the energy starts in the form of, respectively, chemical energy in the muscles, electrical energy in the outlet, and the potential energy in the weight at some height. After transferring into the water, chemical, electrical, and potential energy converts to the thermal energy of water. The water increases temperature. The chemical, electrical, and potential energy are said to *dissipate* into thermal energy.

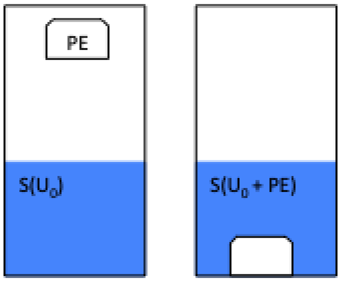
Thermal energy is low-grade energy. We now summarize the facts as follows.

1. Chemical, electrical, and mechanical energy can convert to thermal energy.
2. The conversion of chemical, electrical, and mechanical energy to thermal energy is irreversible.

The dissipation of energy is analogous to the dispersion of ink. The total number of pigment particles is conserved; the particles disperse, rather than stay localized. The total amount of energy is conserved; the energy dissipates into molecular movements, rather than returning the apple to the same height.

The irreversibility of the dissipation of energy is understood from the molecular picture. Thermal energy corresponds to molecular motion, whereas the jumping up of the weight corresponds to all molecules adding velocity in one direction. The former corresponds to more quantum states than the latter. The isolated system changes in the direction that increases the number of quantum states. Consequently, the potential energy dissipates into thermal energy, not the other way around.

To speak of the dissipation of energy, we identify thermal energy and other forms of energy in a single isolated system. The isolated system conserves energy, but dissipates the other forms of energy into thermal energy. So long as the system is isolated, the direction of dissipation is irreversible, from other forms of energy to thermal energy. Thermal energy is called *low-grade energy*.



We next analyze the falling weight into water using the basic algorithm of thermodynamics (BAT).

Step 1. Construct an isolated system with an internal variable. The bottle of water and the weight together constitute an isolated system. Before the weight drops, the thermal energy of water is U_0, and the potential energy of the weight is PE. According to the principle of the conservation of energy, the energy of the isolated system is fixed. After the weight comes to rest in water, the potential energy of the weight vanishes, and the thermal energy of the water is

U_0 + PE. Thus, the thermal energy of the water, U, is an internal variable of the isolated system, increasing from U_0 to U_0 + PE.

Step 2. Find the subset entropy as a function of the internal variable. The bottle of water is a thermal system, characterized by a function S(U), which is an increasing function. Let the entropy of the weight be S_{weight}, which is taken to be unchanged after falling into the water. The entropy of the isolated system is the sum

$S(U) + S_{weight}$.

Step 3. Maximize the subset entropy to reach equilibrium. Before the weight drops, the entropy of the isolated system is $S(U_0) + S_{weight}$. After the weight comes to rest in the water, $S(U_0 + PE) + S_{weight}$. The law of the increase of entropy requires that

$S(U_0 + PE) + S_{weight} > S(U_0) + S_{weight}$.

Because S(U) is an increasing function, the above inequality holds if the potential energy of the weight changes to thermal energy in the water. The potential energy of the weight is said to *dissipate* into the thermal energy in the water. The isolated system maximizes the subset entropy when the potential energy of the weight fully changes to the thermal energy of the water, the weight comes to rest, and the isolated system reaches equilibrium.

Step 4. Increase the subset entropy to see irreversibility. The reverse change would violate the law of the increase of entropy, and therefore violate the fundamental postulate. The weight, after rest in water, will not draw thermal energy from the water and jump up. Dissipation is irreversible. What make thermal energy low-grade energy is its high entropy.

Thus, the dissipation of energy—the conversion of potential energy to thermal energy—results from a basic fact: S(U) of a thermal system is an increasing function.

The Kelvin-Planck statement of the second law of thermodynamics. This analysis confirms an empirical fact. It is impossible to produce no effect other than the raising of a weight by drawing thermal energy from a single thermal system. This fact is called the *Kelvin-Planck statement of the second law of thermodynamics*.

Exercise. Use the basic algorithm to analyze heating water by an electric current.

Exercise. In *Heat considered as a Mode of Motion*, published in 1863, John Tyndall described numerous experiments that tested the hypothesis of thermal energy. Wiki Julius Robert von Mayer. Wiki James Prescott Joule. The following passage is taken from the book by Tyndall.

A bullet, in passing through the air, is warmed by the friction, and the most probable theory of shooting stars is that they are small planetary bodies, revolving round the sun, which are caused to swerve from their orbits by the attraction of the earth, and are raised to incandescence by friction against our atmosphere.

Assignment. Use the basic algorithm to analyze heating by friction. Identify an isolated system with an internal variable x. Identify the function S(x). Interpret equilibrium. Interpret irreversibility.

BAT on thermal contact

Thermal contact. We have just analyzed the dissipation of energy from a high grade to a low grade. We now look at the transfer energy from one thermal system to another thermal system.

Two thermal systems are said to be in *thermal contact* if the following conditions hold.

1. The two thermal systems interact in one mode only: transfer energy.
2. The two thermal systems together form an isolated system.

Facts. The principle of the conservation of energy requires that an isolated system should have a fixed amount of energy. It allows arbitrary partition of energy between the two thermal systems, so long as the sum of the energies of the two thermal systems remains constant. However, our everyday experience indicates two facts:

1. When two thermal systems are in thermal contact, energy transfers from one system to the other system, one-way and *irreversible*.
2. After some time, the energy transfer stops, and the two thermal systems are said to reach *thermal equilibrium*.

We now trace these empirical facts to the fundamental postulate. That is, we run the basic algorithm of thermodynamics (BAT) on thermal contact.

Step 1. Construct an isolated system with an internal variable. The two thermal systems, A and B, together constitute an isolated system. We call this isolated system the *composite*. The composite is an isolated system with one independent internal variable. Let the energies of the two thermal systems be U_A and U_B. According to the principle of the conservation of energy, the isolated system—the composite—has a fixed amount of energy, $U_{composite}$. Energy is an extensive quantity, so that

$$U_{composite} = U_A + U_B.$$

Consequently, the isolated system has a single independent internal variable, say, the energy of one of the thermal systems, U_A.

Step 2. Find the subset entropy as a function of the internal variable. The two thermal systems are characterized by two functions, $S_A(U_A)$ and $S_B(U_B)$. Once the internal variable U_A is fixed, the composite flips among a subset of its quantum states. Denote the subset entropy by $S_{composite}(U_A)$. Entropy is an extensive quantity, so that

$S_{composite}(U_A) = S_A(U_A) + S_B(U_B)$.

Because $U_A + U_B$ is fixed, when thermal system A gains energy, thermal system B loses energy. Because $S_A(U_A)$ are $S_B(U_B)$ both increasing functions, when energy transfers from system A to system B, $S_A(U_A)$ decreases but $S_B(U_B)$ increases. Consequently, the function $S_{composite}(U_A)$ in general is not monotonic.

Step 3. Maximize the subset entropy to reach equilibrium. According to calculus,

$dS_{composite}(U_A) = (dS_A(U_A)/dU_A)dU_A + (dS_B(U_B)/dU_B)dU_B$.

When thermal system A gains energy dU_A, thermal system B loses energy by the same amount, $dU_B = - dU_A$. Write the above equation as

$dS_{composite}(U_A) = (dS_A(U_A)/dU_A - dS_B(U_B)/dU_B)dU_A$.

After being isolated for a long time, the composite reaches equilibrium, and the subset entropy maximizes, $dS_{composite}(U_A) = 0$, so that

$dS_A(U_A)/dU_A = dS_B(U_B)/dU_B$.

This equation is the condition of *thermal equilibrium*, and determines the equilibrium partition of energy between the two thermal systems A and B.

Step 4. Increase the subset entropy to see irreversibility. Prior to reaching equilibrium, the subset entropy of the composite increases in time, $dS_{composite} > 0$. Distinguish two possibilities:

- If $dS_A(U_A)/dU_A > dS_B(U_B)/dU_B$, then $dU_A > 0$, and system A gains energy from system B.
- If $dS_A(U_A)/dU_A < dS_B(U_B)/dU_B$, then $dU_A < 0$, and system A loses energy to system B.

These inequalities dictate the direction of energy transfer. In thermal contact, the direction of energy transfer is one-way and irreversible.

The BAT confirms the two empirical facts of thermal contact.

1. Without loss of generality, assume that, right after thermal contact, $dS_A(U_A)/dU_A > dS_B(U_B)/dU_B$. Our analysis shows that system A grains energy from system B. The direction of the energy transfer is one-way and irreversible.
2. We further assume that $S_A(U_A)$ and $S_B(U_B)$ are convex functions. Consequently, as system A gains energy, the slope $dS_A(U_A)/dU_A$ decreases. As system B loses energy, the slope $dS_B(U_B)/dU_B$ increases. Our analysis shows that the transfer of energy continues

until the two slopes are equal, $dS_A(U_A)/dU_A = dS_B(U_B)/dU_B$, i.e., when the two thermal systems reach thermal equilibrium.

Definition of temperature

Define temperature T by

$1/T = dS(U)/dU$.

A child is born. This definition relates temperature to entropy and energy.

Entropy is an absolute property, but energy is a relative property. Because the definition of temperature only uses the difference in energy, temperature so defined is an absolute property.

Both S and U are extensive thermodynamic properties. The definition makes T an intensive thermodynamic property.

Because entropy is a dimensionless number, $S = \log \Omega$, temperature has the same unit of energy, Joule.

If temperature is in the unit of Kelvin, to maintain the equation $1/T = dS(U)/dU$, the entropy need be in the fake unit of the Boltzmann constant:

$S = k_B \log \Omega$.

The roles of temperature. We can use the word *temperature* to paraphrase the above analysis of thermal contact.

1. When two thermal systems are brought into thermal contact, energy transfers only in one direction, from the system of high temperature to the system of low temperature. This fact is called the *Clausius statement of the second law of thermodynamics*.
2. After some time in thermal contact, energy transfer stops, and the two systems have the same temperature. This fact is called the *zeroth law of thermodynamics*.

Temperature of a thermal system measures the escaping tendency of energy from the system.

Flexibility in defining temperature. But wait a minute! Any decreasing function of dS(U)/dU also serves as a definition of temperature. What is so special about the choice made above? Nothing. It is just a choice. Indeed, all that matters is the slope dS(U)/dU. Nature is indifferent to what humans call this slope.

Range of temperature. For a thermal system, the function S(U) is a monotonically increasing function. The more energy, the more quantum states, and the more entropy. Thus, the definition

$1/T = dS(U)/dU$ makes temperature positive. Usually we only measure temperature within some interval. Extremely low temperatures are studied in the science of cryogenics. Extremely high temperatures are realized in stars, and other special conditions.

Circular statements. What is temperature? Temperature is a property shared by two bodies in thermal contact, when they stop exchanging energy by heat.

What is heat? Heat is the transfer of energy caused by difference in temperature.

The circular statements define neither heat nor temperature. They are correct and useful statements: they link heat and temperature.

Temperature and heat are distinct quantities. We will show that heat and temperature can be determined by separate experiments. The art of measuring heat is called *calorimetry*, and the art of measuring temperature is called *thermometry*.

What can you do for temperature? An essential step to grasp thermodynamics is to get to know the temperature. We define temperature by running BAT on an everyday experience—thermal contact. How does temperature rises up as an abstraction from everyday experience of thermal contact? How does temperature comes down from the union of energy and entropy?

Let me paraphrase a better-known Bostonian. And so, my fellow thermodynamicist: ask not what temperature can do for you—ask what you can do for temperature.

Temperature is not a scalar. Values of temperature do *not* form a scalar set. Whereas two values of energy add to give another value of energy, two values of temperature never add.

We have used temperature-volume plane and energy-volume plane. The former is not a two-dimensional vector space, but the latter is.

Temperature is a child of entropy and energy. The relation between entropy, energy, and temperature was invented by Clausius (1854). At the time of invention, both temperature and energy had been accepted, but entropy was imagined by Clausius. He used energy and temperature to define entropy:

$dS = T^{-1}dU$.

His logic has been adopted in many modern textbooks. Here I do not follow his logic. Instead, following a later development, I regard energy and entropy as primitive quantities, and use them to define temperature. The origin of temperature is obscure until it is related to entropy and energy.

Exercise. Write an essay with the title, *What is the temperature*? How does temperature result from everyday experience of thermal contact? How is temperature born from the union of energy and entropy?

Exercise. Hotness and happiness are two common feelings. We measure hotness by an experimental quantity, temperature. Can we do so for happiness? Why?

Exercise. Replace the word “happiness” in the above exercise with any elusive attribute that people wish to measure, such as intelligence, beauty, and love.

M.W. Zemansky, Temperatures very low and very high, 1964.

M. W. Zemansky, Heat and Thermodynamics (5th.ed.), 1968. An influential textbook with good description of experiments.

Nobel lecture. Onnes, Investigations into the Properties of Substances at Low Temperatures, which Have Led, amongst Other Things, to the Preparation of Liquid Helium, 1913.

Degradation of energy

Grade thermal systems by their temperatures. Thermal energy is low-grade energy: all other forms of energy can transfer into a thermal system. Now we can compare all thermal systems, and give each a grade. When two thermal systems are in thermal contact, the thermal system of a high grade transfers energy to the thermal system of a low grade. The grade of each thermal energy is its temperature.

Degrade energy by transferring energy from a high-temperature thermal system to a low-temperature thermal system. Consider two thermal systems characterized by functions $S_A(U_A)$ and $S_B(U_B)$. In thermal contact, one thermal system transfers energy to the other, but the two thermal systems together constitute an isolated system. The sum of the energies of the two thermal systems is conserved:

$$U_A + U_B = \text{constant}.$$

When the energy can transfer between the two thermal systems, the composite—the isolated system—has a sample space of quantum states. When the energies of the two subsystems are fixed at U_A and U_B, the isolated system flips among a subset of quantum states, and the subset entropy is

$$S_A(U_A) + S_B(U_B).$$

To increase the subset entropy, the energy transfers from a thermal system with a lower slope dS/dU to a thermal system with a higher slope dS/dU. That is, energy degrades by transferring from a high-temperature thermal system to a low-temperature thermal system.

Exercise. Compare dissipation of energy and degradation of energy.

Features of the function T(U) common to all thermal systems

Recall the definition of temperature, 1/T = dS(U)/dU. We plot the function T(U) on the energy-temperature plane. We use energy as the horizontal axis, and temperature as the vertical axis. Each point on the curve represents a thermal system isolated at a particular value of energy. That is, each point on the curve represents a thermodynamic state of the thermal system. Note several general features of the curve T(U).

1. The energy is defined up to an additive constant, so that the curve T(U) can be translated along the axis of energy by an arbitrarily amount.
2. The temperature T starts at absolute zero, is positive, and has no upper bound.
3. For the time being, we assume that T(U) is an increasing function.

These features of T(U) should be compared with those of S(U).

Exercise. A thermal system can also be characterized by function S(T). Discuss the general features of the curve S(T) on the entropy-temperature plane.

Thermal capacity

When the energy of a thermal system changes by dU, the temperature changes by dT. Define the *thermal capacity* by

1/C = dT(U)/dU.

Because energy is an extensive quantity and temperature is an intensive quantity, thermal capacity is an extensive quantity. Thermal capacity is a function of state. When we report temperature in the unit of energy, thermal capacity is dimensionless. When we report temperature in the unit Kelvin, the thermal capacity has the fake unit of entropy, JK^{-1}.

The thermal capacity is a function of energy, C(U). We assume that the thermal capacity is positive. This assumption is equivalent to that the function T(U) has positive slope, and that the function S(U) is convex. Recall the definition of temperature, 1/T = dS(U)/dU.

Thermal capacity is commonly called heat capacity. Thermal capacity is a function of state, and is independent of the method of energy transfer. For example, we can add energy to a half bottle of water by work, such as shaking the bottle, or electric heating. Once we commit to the modern usage of the word heat as a method of energy transfer, it is inappropriate to name a function of state using the word heat.

Specific thermal capacity. The energy needed to raise the temperature of a unit mass of a substance by a degree is called the *specific thermal capacity* of the substance. Liquid water has approximately a constant specific thermal capacity of 4.18 kJ/kg-K. Ice has approximately a constant specific thermal capacity of 2.06 kJ/kg-K.

Exercise. (a) We immerse a 100 W light bulb in 1 kg of water for 10 minutes. Assume that all electric energy applied to the bulb converts to the internal energy of water. How much does the temperature of the water increase? (b) How much does the temperature of the water increase when an apple falls from a height of 1 m into the water and converts all its potential energy to the internal energy of the water? Similar experiments were conducted in 1840s to establish that heat is a form of energy.

Exercise. What are the changes in energy and entropy of 1 kg of water when raised from the freezing to the boiling temperature?

Exercise. When 1 kg of water at the freezing point is mixed with 2 kg of water at the boiling point, what is the temperature in equilibrium? What is the change of entropy associated with this mixing?

Exercise. For a solid or a liquid, the change of volume is small when temperature increases. We model the solid or liquid as a thermal system, and measure the temperature-energy curve experimentally. For a small range of temperature, the thermal energy is approximately linear in temperature, U(T) = CT, where the thermal capacity C is taken to be a constant. Derive the characteristic function S(U).

Calorimetry

The art of measuring thermal energy is called *calorimetry*. A device that measures thermal energy is called a *calorimeter*. Wiki calorimetry.

Calorimetry has become an art of high sophistication. It is too much of a tangent to talk about current practice of calorimetry in a beginning course in thermodynamics. All we need to know is that thermal energy is measured routinely.

This said, it is good to have a specific method in mind. Just think of an electric heater. The electric energy is (current)(voltage)(time), assumed to be fully converted into thermal energy. I have previously described how to measure the function U(T,V) of a fluid in a cylinder-piston setup.

Thermometry

The art of measuring temperature is called *thermometry*. A device that measures temperature is called a *thermometer*. Temperature affects all properties of all materials. In principle, any property of any material can serve as a thermometer. The choice is a matter of convenience, accuracy, and cost. Here are two commonly used thermometers.

Mercury-in-glass thermometer. A mercury-in-glass thermometer relies on a property of mercury: the volume expands as temperature increases. Thus, a volume indicates a temperature.

Gas thermometer. An ideal gas obeys the equation of state:

$PV = Nk_BT$.

This equation relates temperature T to measurable quantities P, V, and N. Thus, an ideal gas can serve as a thermometer, called the *gas thermometer*.

Exercise. Watch a video of a gas thermometer at constant volume. Explain how this thermometer works.

A division of labor. How does a doctor determine the temperature of a patient? Certainly she does not count the enormous number of quantum states of her patient. Instead, she uses a thermometer. Let us say that she brings a mercury-in-glass thermometer into thermal contact with the patient. Upon reaching thermal equilibrium with the patient, the mercury expands a certain amount, giving a reading of the temperature of the patient.

The manufacturer of the thermometer must assign a volume of the mercury to a temperature. This he can do by bringing the thermometer into thermal contact with a flask of an ideal gas. He determines the temperature of the gas by measuring its volume, pressure, and number of molecules. Also, by heating or cooling the gas, he varies the temperature and gives the thermometer a series of markings.

Any experimental determination of the thermodynamic temperature follows these basic steps:

1. For a simple system, formulate a theory that relates temperature to a measurable quantity.
2. Use the simple system to calibrate a thermometer by thermal contact.
3. Use the thermometer to measure temperatures of any other system by thermal contact.

Steps 2 and 3 are sufficient to set up an arbitrary scale of temperature. It is Step 1 that maps the arbitrary scale of temperature to the thermodynamic temperature.

Our understanding of temperature now divides the labor of measuring temperature among a doctor (Step 3), a manufacturer (Step 2), and a theorist (Step 1). Only the theorist needs to count the number of quantum states, and only for very few idealized systems.

Exercise. YouTube temperature sensor. Explain how thermocouple works.

Count the number of quantum states experimentally

This is a magic of thermodynamics. We can count experimentally the number of quantum states of an isolated system of any complexity, knowing nothing about the quantum states themselves. We illustrate the method using a thermal system.

Division of labor. Recall the definition $S = \log \Omega$. Counting the number of quantum states of an isolated system is equivalent to determining its entropy.

Some things are easy to calculate theoretically, others are easy to measure experimentally. A division of labor improves the economics of getting things done. Much of thermodynamics is only sensible in terms of the division of labor between theory and experiment, and between people and machines. For most isolated systems, counting quantum states experimentally is far more economic than computing them theoretically.

Here is a statement of the task. Given a thermal system, measure its characteristic function $S(U)$. Recall the definition of temperature, $dS(U) = T^{-1}dU$. Counting the number of quantum states requires a combination of thermometry to measure T and calorimetry to measure U.

Experimental measurement of the function T(U). We add energy to the thermal system by, say, an electric heater. We measure the change in energy U by $(\text{time})(\text{resistance})(\text{current})^2$. At each increment of energy, we isolate the system, wait until the system reaches equilibrium, and measure temperature T. These incremental measurements determine the function $T(U)$.

Determination of entropy. Recall the definition of temperature:

$$dS(U) = T^{-1}dU.$$

This equation relates the function $S(U)$ to experimentally measurable quantity, U and T. Once the function $T(U)$ is measured experimentally, an integration determines the function $S(U)$.

In this integration, set $S = 0$ as $T \to 0$. That is, at the ground state, the number of quantum states is low, and is set to be one. This is a statement of *the third law of thermodynamics*. On the energy-entropy plane, the curve $S(U)$ approaches the horizontal axis vertically.

Often, the measurement only extends to a temperature much above absolute zero. Assume that the measurement gives the energy-temperature curve in the interval between T_0 and T. Upon integrating, we obtain the relative entropy, $S(T) - S(T_0)$. Such an experiment leaves the absolute entropy undetermined.

Recall that the function S(U) characterize the thermal system as a family of isolated systems. Thus, we can count the number of quantum states of each member isolated system in the family.

Entropy and thermal capacity. Recall the definitions $dS = T^{-1}dU$ and $C(T) = dU(T)/dT$. Regard entropy as a function of temperature, S(T), so that

$dS(T)/dT = C(T)/T$.

The function C(T) is often determined by concurrent measurements of temperature and energy, so that $C(T) = dU(T)/dT$. Once C(T) is determined in a range of temperature from T_0 and T, the above equation is integrated to obtain $S(T) - S(T_0)$.

Debye model

To illustrate the determination of the characteristic function S(U), consider the Debye model (1912). Near absolute zero, the internal energy of a solid takes the form

$U = aT^4$,

where a is a constant. Debye obtained this expression from a microscopic model. Here we regard the U(T) as a curve obtained from experimental measurements.

Invert the above equation, and we have $T = (U/a)^{1/4}$. Integrating $dS = T^{-1}dU$, we obtain that

$S(U) = (4/3)a^{1/4}U^{3/4}$.

We have used the condition S = 0 at T = 0.

Exercise. Calculate the function C(T) for the Debye model.

Nobel lecture. Debye, Methods to Determine the Electrical and Geometrical Structure of Molecules, 1936.

BAT on melting

Model melting using a thermal system

We now trace the experimental observation of melting back to the fundamental postulate. We model a fixed amount of a pure substance as a thermal system. This model assumes that the pure substance can change energy, but ignores that the pure substance can also change volume. The thermal-system model is an approximation for solid and liquid, but not for gas.

Primitive curves

Consider a pure substance of two phases, A and B. We model phase A as a thermal system of characteristic function $s_A(u_A)$, where u_A is the energy per molecule, and s_A is the entropy per molecule. Similarly, we model phase B as a thermal system of characteristic function $s_B(u_B)$. In the energy-entropy plane, $s_A(u_A)$ and $s_B(u_B)$ are two curves, called the *primitive curves* of the pure substance. Each point on a primitive curve corresponds to a *homogeneous state* of the pure substance.

A mixture of two homogeneous states

We now consider a mixture of two homogeneous states: state (u_A,s_A) is a point on one primitive curve, and state (u_B,s_B) is a point on the other primitive curve.

Number fraction. The mixture has a total of N molecules, of which N_A molecules are in homogeneous state A, and N_B molecules are in homogeneous state B. Denote the number fractions of the molecules in the two homogeneous states by

$y_A = N_A/N, \ y_B = N_B/N.$

Both y_A and y_B are nonnegative numbers. The number of molecules in the mixture is conserved:

$N = N_A + N_B.$

Dividing the above equation by N, we obtain that

$y_A + y_B = 1.$

Rule of mixture. The mixture is also a thermal system. Let u be the energy of the mixture divided by the total number of molecules in the mixture. Energy is an extensive variable, so that the energy of the mixture is the sum of the energies of the two homogeneous states:

$Nu = N_A u_A + N_B u_B$.

Dividing the above equation by N, we obtain that

$u = y_A u_A + y_B u_B$.

This equation is a *rule of mixture*. The same is true for entropy:

$s = y_A s_A + y_B s_B$.

Here s is the entropy of the mixture divided by the number of molecules in the mixture.

Graph the rule of mixture. These rules of mixture can be graphed on the energy-entropy plane. Homogeneous state A is a point (u_A,s_A) on the primitive curve $s_A(u_A)$. Homogeneous state B is a point (u_B,s_B) on the primitive curve $s_B(u_B)$. The mixture is a point (u,s) on the line segment joining the two points (u_A,s_A) and (u_B,s_B), located at the center of gravity, depending on the fraction of molecules y_A and y_B allocated to the two phases. In general, the mixture (u,s) is a point off the primitive curves, and may not be a state of equilibrium.

Neglect the spatial arrangement of pieces of homogeneous states. The rules of mixture depend on the number of molecules in each homogenous state, but not on how the pieces of homogenous states are arranged in space.

The rules of mixture also neglect molecules at the interfaces between pieces of homogenous states. The molecules at the interfaces have their own thermodynamic properties, different from those of the homogeneous states. The interfaces contribute to energy and entropy negligibly, so long as the pieces of the homogenous states are much larger than the size of individual molecules.

A mixture of any number of homogeneous states

Number fractions. Now consider a mixture of any number of homogenous states. The homogeneous states can be on one primitive curve, or on both primitive curves. For example, consider a mixture of three homogeneous states, A, B, and C. A pure substance has a total of N molecules, of which N_A, N_B, and N_C molecules are in the three homogeneous states. Denote the number fractions by

$y_A = N_A/N$, $y_B = N_B/N$, and $y_C = N_C/N$.

Here y_A, y_B and y_C are non-negative numbers. The mixture conserves the number of molecules:

$N_A + N_B + N_C = N$.

Divide this equation by N, and we obtain that

$y_A + y_B + y_C = 1$.

Rule of mixture. The energy and energy per molecule of the mixture, (u,s), are given by

$u = y_A u_A + y_B u_B + y_C u_C$,
$s = y_A s_A + y_B s_B + y_C s_C$.

Graph the rule of mixture. The three homogeneous states, (u_A,s_A), (u_B,s_B), and (u_C,s_C), are three points on one or two primitive curves. The three points form a triangle in the energy-entropy plane. The mixture, (u,s), is a point in the energy-entropy plane, located at the center of gravity in the triangle, depending on the fraction of molecules $y_{A,}$ y_B and y_C allocated to the three homogeneous states at the vertices of the triangle. In general, the mixture (u,s) is a point off the primitive curves.

Convex hull

Each point on the primitive curves corresponds to a homogenous state. A mixture corresponds to a point at the center of gravity of some number of homogeneous states. All possible mixtures of arbitrary numbers of homogeneous states constitute a region in the energy-entropy plane. Each mixture in the region may not be a state of equilibrium.

Incidentally, in the language of *convex analysis*, the energy-entropy plane is called a *vector space*, and each point in the plane is called a *vector*. All the homogeneous states on the primitive curves define a set of vectors. The vector representing a mixture is a linear combination of the vectors representing the homogeneous states. In the linear combination, every coefficient is nonnegative, and all coefficients sum to 1. Such a linear combination is called a *convex combination*, The set of all mixtures is called the *convex hull* of the homogenous states.

Derived curve

The region of all possible mixtures (i.e., the convex hull) is bounded from above by a single curve, called the *derived curve*.

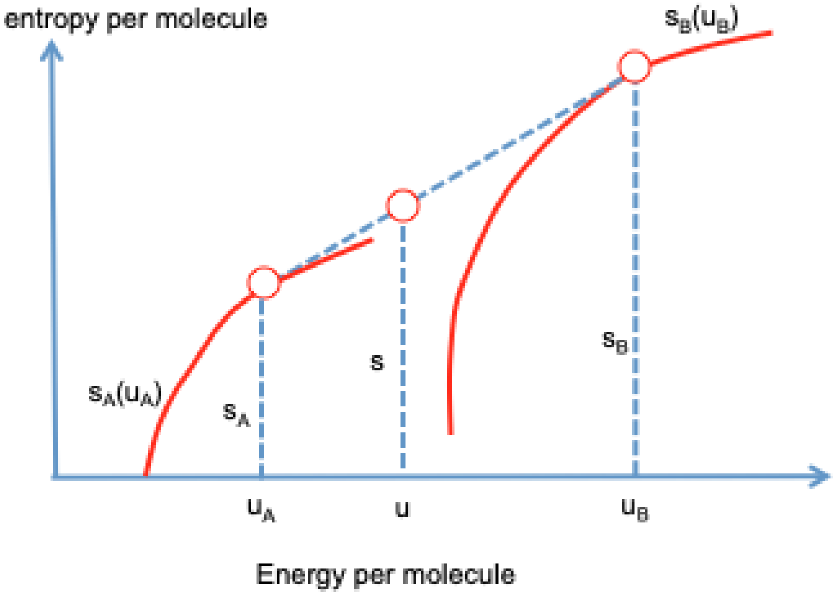
The derived curve is formed by rolling tangent lines on the primitive curves. A tangent line can touch the primitive curves at one point or two points, but not three or more points. The derived curve is convex.

So far energy and entropy play similar roles: they are extensive properties. We next apply the basic algorithm of thermodynamics.

A fixed amount of mixture of a fixed amount of energy is an isolated system. The isolated system has an enormous number of internal variables: the number of single-phase states, the location of each single-phase state on a primitive curve, and the number fraction of molecules allocated to each phase. The entropy of the mixture is the subset entropy, which is a function of all the internal variables.

The isolated system has a fixed amount of energy u, represented by a vertical line on the energy-entropy plane. The vertical line intersects the derived curve at one point, which maximizes the subset entropy.

As the energy of a pure substance varies, the derived curve represents all thermodynamic states of the pure substance.



Equilibrium of a single homogeneous state

If a line tangent to one point on a primitive curve does not cut any primitive curves, this point belongs to the derived curve. The set of all such points is called the *curve of absolute stability*. The tangent line can roll on the primitive curve to change the slope of the tangent line. Thus, the curve of absolute stability has one degree of freedom. Recall 1/T = ds(u)/du. The slope of the tangent line corresponds to temperature.

Equilibrium of two homogeneous states

If a line tangent to two points on the primitive curves does not cut any primitive curves, the straight-line segment connecting the two tangent points belongs to the derived curve. The straight-line segment is called a *tie line*. The common tangent line cannot roll on the primitive curves, is fixed in the energy-entropy plane, and has no degree of freedom. The two tangent points at the ends of the tie line are called the *limits of absolute stability*.

Let the tangent line touch one primitive curve $s_A(u_A)$ at point (u_A,s_A), and touch the other primitive curve $s_B(u_B)$ at point (u_B,s_B). The two tangent points correspond to the two homogeneous states in equilibrium. The slope of the tangent line defines the melting temperature. Thus,

$$1/T_m = (s_B - s_A)/(u_B - u_A) = ds_B(u_B)/du_B = ds_A(u_A)/du_A.$$

Given the two primitive curves, $s_A(u_A)$ and $s_B(u_B)$, the above equations solve for the melting temperature T_m, as well as the two homogeneous states in equilibrium, (u_A,s_A) and (u_B,s_B).

Equilibrium of three homogenous states does not exist in the thermal-system model

The three phases of H_2O—ice, water, and steam—can equilibrate. The three-phase equilibrium, however, cannot be represented by the thermal-system model.

In the thermal-system model, each phase is represented on the energy-entropy plane by a curve—a primitive curve. Three phases are represented by three primitive curves. A straight line rolling over the three primitive curves can at once touch one primitive curve or two primitive curves, but not three primitive curves. The exception is that all three primitive curves are exactly positioned to have a common tangent line. The chance for such an exception is negligible.

Temperature-entropy curve

Ice melts at temperature 273.15 K. At the melting temperature, the specific thermal capacity for ice is c_s = 2.06 kJ/kg/K. Thus, for ice near the melting temperature, we have

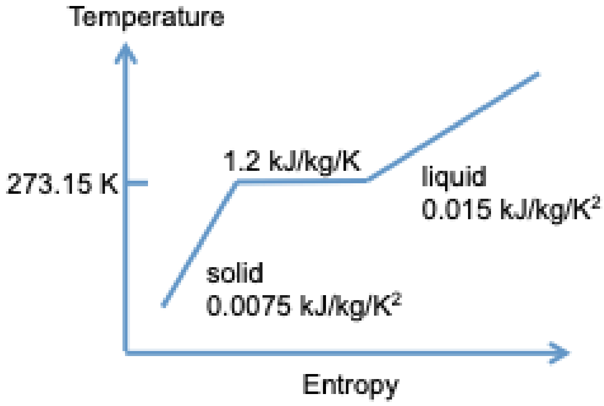
$$ds(T)/dT = c_s/T_m = (2.06\ \mathrm{kJ/kg/K})/(273.15\ \mathrm{K}) = 0.0075\ \mathrm{kJ/kg/K^2}.$$

At the melting temperature, the specific thermal capacity for liquid water is c_f = 4.18 kJ/kg/K. Thus, for liquid water near the melting temperature, we have

$$ds(T)/dT = c_f/T_m = (4.18\ \mathrm{kJ/kg/K})/(273.15\ \mathrm{K}) = 0.015\ \mathrm{kJ/kg/K^2}.$$

Recall that $s_f - s_s = (u_f - u_s)/T_m$. The specific energy of phase change is 334 kJ/kg. The specific entropy of phase change is

$$s_f - s_s = (334\ \mathrm{kJ/kg})/(273.15\ \mathrm{K}) =1.2\ \mathrm{kJ/kg/K}.$$



Exercise. Can the model of thermal system describes three homogenous states in equilibrium?

Exercise. For water, we have sketched curves T(u) and T(s) near the melting temperature. Now calculate and sketch the curve s(u) near the melting temperature.

Exercise. For water, the melting temperature is 273.15 K, the specific energy of phase transition is 334 kJ/kg. Calculate the ratio of the number of quantum states in the liquid to that in the solid.

Thermal system of a nonconvex characteristic function s(u)

In hindsight, we should not have accepted so readily that the characteristic function of a thermal system, s(u), is a convex function, or that u(T) is an increasing function, or that thermal capacity is positive. In fact, a thermal system may have a nonconvex primitive curve s(u). We can form a tangent line touching two points on the curve s(u). The two points correspond to equilibrium of two homogeneous states.

It turns out that a solid-liquid transition is modeled with two convex primitive curves, but a liquid-gas transition is modeled with a single nonconvex primitive curve. We will see this effect clearly later in a model that allows the pure substance to vary both energy and volume.

Metastability

A primitive curve may contain a convex part and a non-convex part. The point separating the two parts is called the *inflection point* in calculus, and is called the *limit of metastability* in thermodynamics.

If a convex part of the primitive curve lies below the derived curve, the part of the primitive curve is beyond the limit of absolute stability. Each point of this part of the primitive curve is called a *metastable state*. A metastable state is stable in regard to continuous changes of state, but is unstable in regard to discontinuous changes of state.

Exercise. Watch a video on supercooled water. What is supercooled water? How does it form? Indicate supercooled water in a sketch of the primitive curves on the energy-entropy plane. Indicate supercooled water in a sketch of the energy-temperature plane.

Isothermal process

Temperature as an independent variable

A thermal system has a single independent variation. So far we have specified the thermodynamic states of the thermal system using energy. Any one of the functions of state can serve as an independent variable. A popular choice is temperature.

For the time being, we assume that the function T(U) is an increasing function. That is, on receiving energy, a thermal system increases temperature. Any monotonic function is invertible. Write the inverse function as U(T). The two functions, U(T) and T(U), correspond to the same curve on the energy-temperature plane, and contain the same information.

Thermostat

A thermostat is a device that measures temperature and switches heating or cooling equipment on, so that the temperature is kept at a prescribed level. Thermostats are widely used in refrigerators and home-heating and -cooling units.

Sous-vide (/suːˈviːd/; French for "under vacuum") is a method of cooking. Food (e.g., a piece of meat) is sealed in an airtight plastic bag, and placed in a water bath for a longer time and at a lower temperature than those used for normal cooking. The temperature is fixed by a feedback system. Because of the long time and low temperature, sous-vide cooking heats the food evenly; the inside is properly cooked without overcooking the outside. The airtight bag retains moisture in the food.

Thermal reservoir

A thermal reservoir is a thermal system of a fixed temperature. We use the thermal reservoir to fix the temperature of another thermal system by thermal contact. The other thermal system has a much smaller thermal capacity than the thermal reservoir, so that the temperature of the reservoir, T_R, is fixed as the thermal reservoir and the other thermal system exchange energy. In thermal equilibrium, the other thermal system has the same temperature as the thermal reservoir.

We can realize a thermal reservoir by using a large tank of water. When water loses or gains a small amount of thermal energy, the temperature of water is nearly unchanged.

The situation is analogous to a water reservoir. A water reservoir has a lot of water. Its water level remains nearly unchanged when we take a small cup of water from the reservoir.

The thermal reservoir is a thermal system, and interacts with the rest of the world in one mode: transfer energy. When the energy of the reservoir is fixed at a value U_R, the reservoir becomes an isolated system, and has a certain number of quantum states, $\Omega_R(U_R)$. As U_R varies, the function $\Omega_R(U_R)$, or its equivalent, $S_R(U_R) = \log \Omega_R(U_R)$, characterizes the reservoir as a family of isolated systems.

When the reservoir is in thermal contact with a small thermal system, the composite of the reservoir and the system is an isolated system and has a constant energy, $U_{composite}$. Let U be the energy of the small thermal system. The energy of the composite is a sum of parts:

$U_{composite} = U_R + U$.

Recall the definition of temperature, $1/T_R = dS_R(U_R)/dU_R$. Because T_R is constant, integrating, we find that

$S_R(U_R) = S_R(U_{composite}) - (U_{composite} - U_R)/T_R$.

Thus, a thermal reservoir is a thermal system characterized by a linear function $S_R(U_R)$.

BAT on an isothermal process

A process that occurs at a constant temperature is called an *isothermal process*. For example, the sous-vide cooking in an isothermal process. The temperature is fixed while the food cooks. We can fix the temperature by a thermostat, or by a thermal reservoir. So far as the food is concerned, the method of fixing temperature makes no difference. We next run the BAT on an isothermal process.

Step 1. Construct an isolated system with internal variables. A system undergoing an isothermal process is modeled as a thermal system of two variables: energy U and an internal variable x. When both U and x are fixed, the thermal system is an isolated system having a certain number of quantum states, $\Omega(U,x)$. Let $S(U,x) = \log \Omega(U,x)$.

The thermal system is in thermal contact with a thermal reservoir of a fixed temperature T_R. The composite of the thermal system and the reservoir is an isolated system. The isolated system conserves energy, so that the total energy of the composite is fixed, $U_{composite}$. When the thermal system has energy U, the reservoir has energy $U_R = U_{composite} - U$. The isolated system has two independent internal variables, U and x.

Step 2. Calculate the subset entropy of the isolated system as a function of the internal variables. When U and x are fixed, the thermal system has the entropy S(U,x). The reservoir is a thermal system characterized by a function $S_R(U_R)$. The reservoir has a fixed temperature T_R, so that the entropy of the reservoir is linear in U, $S_R(U_{composite}) - U/T_R$, where $S_R(U_{composite})$ is constant.

The subset entropy of the composite is the sum of the entropies of the reservoir and the system:

$S_{composite} = S(U,x) + S_R(U_{composite}) - U/T_R$.

The subset entropy is a function of two independent variables, $S_{composite}(U,x)$.

Step 3. Maximize the subset entropy of the isolated system to reach equilibrium. Of the two internal variable, U and x, we first fix x and let U vary. The isolated system is in thermal equilibrium, so that $\partial S_{composite}/\partial U = 0$. This condition recovers a familiar condition:

$1/T_R = \partial S(U,x)/\partial U$.

That is, in thermal equilibrium, the reservoir and the thermal system have the same temperature, T_R.

We will drop the subscript R and write the temperature as T in the following. The function S(U,x) is known, the above condition of thermal equilibrium defines the function U(T,x). We can also write the entropy as a function S(T,x).

Step 4. Increase the subset entropy of the isolated system to see irreversibility. The energy of the composite $U_{composite}$ is fixed, so that $S_R(U_{composite})$ is a constant. The composite is an isolated system of a single internal variable, x. The BAT proceeds to change x to increase $S_{composite}$, or equivalently, increase the function

$S(T,x) - U(T,x)/T$.

The first term is the entropy of the thermal system, and the second term is the change in the entropy of the reservoir.

Massieu function

Denote the above function by

$J(T,x) = S(T,x) - U(T,x)/T$.

The function was introduced by Massieu (1869). Here S(T,x) and U(T,x) are the entropy and energy of the thermal system. In the isothermal process, the temperature T is not a variable, but is fixed by the temperature of the thermal reservoir. The internal variable x can change.

Aside from an additive constant, the Massieu function is the subset entropy of an isolated system: the composite of a thermal system and a thermal reservoir. The first term is the entropy of the thermal system, and the second term is the change in the entropy of the thermal reservoir. The Massieu function is also called *free entropy*.

Algorithm of thermodynamics for isothermal process. We now paraphrase the basic algorithm of thermodynamics for an isothermal process.

1. Construct a thermal system with an internal variable x, in thermal contact with a thermal reservoir of a fixed temperature T.
2. Identify the function J(T,x) = S(T,x) - U(T,x)/T, where S(T,x) and U(T,x) are the entropy and energy of the thermal system.
3. *Equilibrium*. Find the value of the internal variable x that maximizes the function J(T,x).
4. *Irreversibility*. Change the value of the internal variable x in a sequence that increases the function J(T,x).

Exercise. Use the Massieu function to derive the relation between the melting temperature, the energy of melting, and the entropy of melting.

Helmholtz function

In an isothermal process, the temperature is constant (and positive), maximizing the J(T,x) is the same as minimizing the following function:

$F = U - TS$.

This function is written as F(T,x). This function contains quantities of the thermal system alone, and is called the *Helmholtz function*, or *free energy*. The function was introduced by Gibbs (1875). Note that U has an arbitrary additive constant, which also appears in F.

Observe that F = - JT. When the system is held at a fixed temperature (i.e., in thermal equilibrium with the reservoir), of all values of the internal variable x, the most probable value minimizes the Helmholtz function F(T,x). In this minimization, temperature is not a variable, but is fixed by the thermal reservoir.

Shadow of the real thing. The Helmholtz function comes from the subset entropy of an isolated system: the combination of a system and a thermal reservoir. The Helmholtz function contains no new fundamental principle, and is a shadow of entropy. In practicing thermodynamics, the Helmholtz function is so commonly used that many people are enamored by the shadow, and forget the real thing—entropy.

We can paraphrase the algorithm of thermodynamics for isothermal process in using the Helmholtz function F(T,x), analogous to the algorithm using the Massieu function J(T,x).

Derivative of Helmholtz function. At fixed x, dF = dU - TdS - SdT. Recall the definition of temperature, dU = TdS. We have that

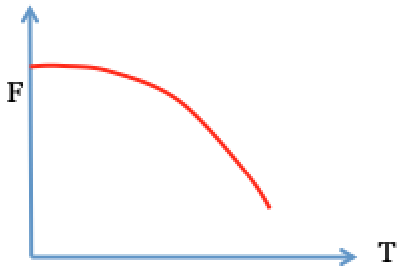
dF = - SdT.

Thus,

- S = ∂F(T,x)/∂T.

Features of the Helmholtz function. For a fixed x, F(T,x) is a function of T. We note the following features of this function as a curve on the F-T plane.

1. F is relative, so that the curve can translate up and down without affecting the behavior of the system.
2. T is absolute. The curve cannot translate left and right.
3. S approaches zero as T approaches zero, so that the curve starts horizontal.
4. Because S is positive, F decreases as T increases.
5. Because S increases as T increases, F is a convex function of T.



Melting analyzed using the Helmholtz function

Let the Helmholtz function per molecule in the solid be $f_A(T)$, and that in the liquid be $f_B(T)$. The Helmholtz function per molecule in a mixture of solid and liquid is

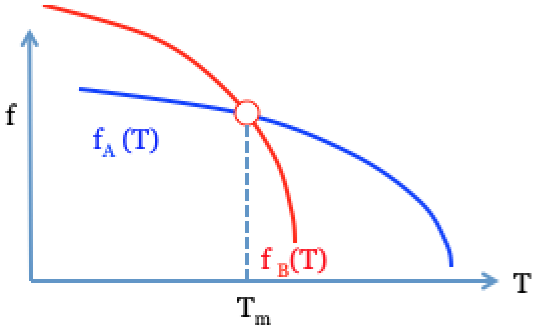
$f = y_A f_A(T) + y_B f_B(T)$.

The change of phase is modeled as an isothermal process. Recall that $y_A + y_B = 1$. The fraction of molecules in the solid, y_A, is the independent internal variable, which is varied to minimize the Helmholtz function of the mixture.

The two curves $f_A(T)$ and $f_B(T)$ are decreasing and convex functions. The equation

$f_A(T) = f_B(T)$.

determines the melting temperature T_m. When $T < T_m$, the Helmholtz function of the mixture minimizes if all molecules freeze. When $T > T_m$, the Helmholtz function of the mixture minimizes if all molecules melt.



Recall the definition of the Helmholtz function, $f = u-Ts$. The condition of equilibrium of the solid and liquid gives that

$u_A - T_m s_A = u_B - T_m s_B$.

This expression recovers what we have obtained before. The Helmholtz function gives us a slick derivation of the equilibrium condition, but pushes us a step away from the leading role—entropy.

Closed system

Now enters a second supporting role—*volume*. In thermodynamics, energy and volume play analogous supporting roles.

A family of isolated systems of two independent variables

A closed system and its surroundings do not transfer matter, but transfer energy and volume.

Consider a half cylinder of water sealed with a piston. Above the piston is a weight, and beneath the cylinder is a fire. Inside the cylinder, liquid occupies some volume, and vapor occupies the rest. The water molecules inside the cylinder, both in the liquid and in the gas, constitute a closed system.

Characteristic function S(U,V). Let U be the energy and V be the volume of a closed system. When the energy U and volume V are fixed, the closed system becomes an isolated system. Denote the number of quantum states of this isolated system by Ω(U,V). As U and V vary, the function Ω(U,V), or its equivalent, S(U,V) = log Ω(U,V), characterizes the closed system as a family of isolated systems. The family has two independent variables, U and V.

For the half cylinder of water, we fix U and V by thermally insulate the cylinder and lock the position of the piston.

A closed system unites entropy, energy, and space. We call the function S(U,V) the characteristic function of the closed system.

Thermodynamic state of a closed system. A closed system is a family of isolated systems. Each member isolated system, after being isolated for a long time, reaches equilibrium. The isolated system in equilibrium defines a *thermodynamic state of the closed system*. A thermodynamic state is synonymous to a member isolated system in equilibrium.

Thermodynamic process of a closed system. A thermodynamic process is synonymous to a sequence of member isolated states, each being in equilibrium. A closed system is a family of isolated systems. A thermodynamic process of the closed system is a subfamily of isolated systems. Because the closed system is characterized by two independent variables, there are infinitely many types of thermodynamic processes.

Energy-volume plane

Energy U and volume V are two scalars. A pair of the values of energy and volume (U,V) is a vector. The set of all pairs of energy and volume forms a two-dimensional vector space.

In a plane, draw one axis to represent energy, and another axis to represent volume. By convention, draw the two axes perpendicularly. Energy and volume play analogous roles of equal importance. Either energy or volume can be the horizontal axis.

A thermodynamic state of a closed system is specified by fixed values of the two thermodynamic properties, U and V. In the energy-volume plane, a point represents a thermodynamic state, and a curve represents a thermodynamic process.

Energy-volume-entropy space

Energy, volume, entropy are three scalars. A list of three values (U,V,S) is a three-dimensional vector. The set of all such vectors forms a three-dimensional vector space.

Drawing a three-dimensional vector space on a piece of paper is hard, but the picture is so suggestive that we fake. Imagine a three-dimensional space, with energy and volume as the horizontal axes, and entropy as the vertical axis. We sketch the imagined three-dimensional space on a piece of paper. We draw the two supporting roles, energy U and volume V, as two horizontal axes. We draw the leading role, entropy S, as the vertical axis.

S(U,V) surface and tangent plane. The characteristic function of a closed system, S(U,V), is a *surface* in the energy-volume-entropy space. The idea of characterizing a closed system by a surface S(U,V) in the energy-volume-entropy space comes from Gibbs (1873).

For a function of two variables, S(U,V), recall a fact of calculus:

$$dS(U,V) = (\partial S(U,V)/\partial U)dU + (\partial S(U,V)/\partial V)dV.$$

Further recall the meanings of the two partial derivatives in calculus:

$$\partial S(U,V)/\partial U = (S(U + dU,V) - S(U,V))/dU,$$
$$\partial S(U,V)/\partial V = (S(U,V + dV) - S(U,V))/dV.$$

Draw a plane tangent to the surface at a point on the surface S(U,V). The tangent plane has the slope $\partial S(U,V)/\partial U$ with respect to the U axis, and the slope $\partial S(U,V)/\partial V$ with respect to the V axis. We next interpret the two partial derivatives of the function—the two slopes at a point on the surface—in terms of experimental measurements.

Constant-volume process

When the volume V is constant and the energy U is variable, the closed system becomes a thermal system. For the half cylinder of water, we lock the position of the piston, so that the volume in the cylinder is fixed. We allow the water to receive energy from the fire, so that the energy in the cylinder is varied. In the energy-volume plane, the constant-volume process corresponds to a line parallel to the energy axis.

For a thermal system, we have defined temperature T by

$$1/T = \partial S(U,V)/\partial U.$$

This equation relates one partial derivative $\partial S(U,V)/\partial U$ to an experimentally measurable quantity—temperature T.

Adiabatic process

We next look at the other partial derivative, $\partial S(U,V)/\partial V$. We make both the cylinder and the piston using materials that block the transfer of matter and block the transfer of energy by heat. But we can move the piston and transfer energy by work.

When a closed system transfers energy with its surroundings by work but not by heat, the closed system is said to undergo an *adiabatic process*.

When we add weights, the gas loses volume but gains energy. Adding weights compresses the gas and causes *adiabatic heating*. When we remove weights, the gas gains volume but loses energy. Removing weights expands the gas and causes *adiabatic cooling.*

The half cylinder of water and the weight together constitute an isolated system. The isolated system has two internal variables, the volume of the cylinder, V, and the energy in the water molecules, U. In an adiabatic process, the two internal variables are related. The piston is assumed to move with no friction. Let P be the pressure inside the cylinder, and A be the area of the piston. The weight applies a force to the piston, PA. When the piston moves up by a distance dz, the volume inside the cylinder increases by $dV = Adz$, the potential energy of the weight increases by $PAdz = PdV$, and the energy of the water increases by dU. The energy of the isolated system is the sum of the thermal energy of the water and the potential energy of the weight. The isolated system conserves energy, so that $dU + PdV = 0$. This equation relates the two internal variables U and V.

When the piston moves, the height of weight changes, but the entropy of the weight, S_{weight}, does not change. At fixed U and V, the entropy of the isolated system is the sum of the entropy of the water molecules and the entropy of the weight: $S(U,V) + S_{weight}$. When U and V vary, the subset entropy maximizes in equilibrium, so that $T^{-1}dU + (\partial S(U,V)/\partial V)dV = 0$. The isolated system undergoes an isentropic process.

This isentropic condition, together with the conservation of energy, $dU + PdV = 0$, yields that

$P/T = \partial S(U,V)/\partial V$.

This equation relates the partial derivative $\partial S(U,V)/\partial V$ to experimentally measurable quantities—pressure P and temperature T. The ratio P/T is the child of the union of entropy and volume, just as the temperature is the child of the union of entropy and energy. Pressure is an intensive thermodynamic property.

Exercise. When I stretch a rubber band rapidly, energy has no time to diffuse out, and the rubber band approximately undergoes adiabatic heating. My lips can feel an increase of the temperature of the rubber band. After some time, some energy does diffuse out, and the temperature of the rubber band becomes the same as that of my lips. When I rapidly release the stretch, the rubber band approximately undergoes adiabatic cooling, and my lips feel a decrease in temperature. Try these experiments yourself.

Experimental determination of the function S(U,V) of a closed system

For the function of two variables, S(U,V), calculus dictates that

$$dS = (\partial S(U,V)/\partial U)dU + (\partial S(U,V)/\partial V)dV$$

We have related the two partial derivatives to temperature and pressure, so that

$$dS = (1/T)dU + (P/T)dV.$$

This equation relates the characteristic function S(U,V) to experimentally measurable quantities, U, V, P, T. By incrementally changing the energy and volume, we can measure the function S(U,V). In integrating entropy, recall that entropy is absolute: $S(U,V) = 0$ as $T(U,V) \rightarrow 0$.

The function S(U,V) characterize the closed system as a family of isolated systems. Thus, we can experimentally count the number of quantum states for each member isolated system in the family.

Exercise. Gibbs (1873) wrote $dU = TdS - PdV$. Confirm that this equation is equivalent to the equation $dS = (1/T)dU + (P/T)dV$.

BAT on two closed systems in contact

Two closed systems, A and B, are said to be in contact when they exchange energy and volume, but not matter. We now run the BAT on the two closed systems in contact.

Step 1. Construct an isolated system with internal variables. System A is characterized by a function $S_A(U_A,V_A)$, and system B is characterized by another function $S_B(U_B,V_B)$. We make the composite of the two closed systems into an isolated system. The principles of conservation of energy and space require that

$U_A + U_B$ = constant,
$V_A + V_B$ = constant,

The composite is an isolated system of two independent internal variables: U_A and V_A.

Changes of the internal variables satisfy the following relations:

$dU_A + dU_B = 0$,
$dV_A + dV_B = 0$.

Step 2. Calculate the subset entropy of the isolated system as a function of the internal variables. When the independent internal variables U_A, V_A are fixed at particular values, the isolated system flips in a subset of the sample space. Denote the subset entropy by $S_{composite}(U_A, V_A)$. Entropy is an extensive quantity, so that the subset entropy is a sum:

$S_{composite}(U_A, V_A) = S_A(U_A, V_A) + S_B(U_B, V_B)$.

When the internal variables change by dU_A, dV_A, the subset entropy changes by

$dS_{composite} = (1/T_A - 1/T_B)dU_A + (P_A/T_A - P_B/T_B)dV_A$.

Step 3. Maximize the subset entropy to reach equilibrium. The internal variables U_A and V_A can change independently. In equilibrium, the subset entropy maximizes, $dS_{composite} = 0$, so that

$T_A = T_B$,
$P_A = P_B$.

Equilibrium requires two conditions: the two closed systems have the equal temperature and equal pressure.

Step 4. Change the internal variable to increase the subset entropy; irreversibility. Out of equilibrium, the BAT requires that the subset entropy should increase as time progresses, $dS_{composite} > 0$.

Consider a situation where the two closed systems are in thermal equilibrium, $T_A = T_B$, but not in equilibrium with respect to the transfer of volume. The inequality $dS_{composite} > 0$ reduces to

$(P_A - P_B)dV_A > 0$.

When $P_A > P_B$, the BAT requires that $dV_A > 0$. That is, when two closed systems in contact and in thermal equilibrium, the system of high pressure gains volume from the system of low pressure.

The BAT keeps track of energy and volume, and does not need the hair-splitting definition of work and heat.

Features of the function S(U,V) common to all closed systems

Note the following features of the surface S(U,V) common to all closed systems.

1. Because energy is relative to an arbitrary reference, the surface S(U,V) can translate in the direction of energy by an arbitrary amount without affecting the behavior of the closed system.

2. Because entropy is absolute, the surface starts at $S = 0$, and cannot be translated up and down.
3. Volume is also absolute and positive.
4. When a plane is tangent to the surface $S(U,V)$ at a point, the two slopes of the tangent plane represent $1/T$ and P/T.
5. For each fixed V, as S approaches zero, $S(U,V)$ is a curve that approaches the U axis vertically. That is, $\partial S(U,V)/\partial U$ approaches infinity as S approaches zero.
6. The more energy and volume, the more quantum states. Thus, $\Omega(U,V)$ is an increasing function with respect to both U and V. Because logarithm is an increasing function, $S(U,V)$, is also an increasing function. That is, the slopes $\partial S(U,V)/\partial U$ and $\partial S(U,V)/\partial V$ are positive.
7. For the time being, we assume that $S(U,V)$ is a *convex function*.

Thermal capacity

Given a closed system, a thermal capacity C is defined as the energy received by heat Q per unit increase in temperature T:

$C = \partial Q/\partial T$.

The quantity of heat Q is not a property, but depends on process. Let us look at two processes.

Constant-volume thermal capacity. In a constant-volume process, the closed system becomes a thermal system. For example, a rigid bottle containing a fixed amount of fluid is a thermal system. As the fluid receives energy from the surroundings, the internal energy U of the fluid increases.

Specify the states of the closed system by two independent variables, temperature T and volume V. The internal energy of the closed system is a function of state, $U(T,V)$. When the closed system receives energy in a constant-volume process, define the *constant-volume thermal capacity* by

$C_V = \partial U(T,V)/\partial T$.

The constant-volume thermal capacity is a function of state, $C_V(T,V)$—a property of the closed system.

Exercise. Show that $\partial S(T,V)/\partial T = C_V/T$.

Constant-pressure thermal capacity. When a closed system undergoes a constant-pressure process, we picture the closed system as a cylinder-piston setup enclosing a fixed amount of fluid, subject to a constant weight, and placed over a fire. The fixed amount of fluid in the cylinder and the constant weight above the piston together constitute a thermal system. As the fluid receive energy from the fire, the internal energy U of the fluid increases.

The internal energy of the composite—the fluid in the cylinder and the weight above the piston—is the sum of the internal energy of the fluid and the potential energy of the weight, U + PV. We have called this sum the enthalpy of the closed system, H = U + PV.

Specify the states of the closed system by two independent variables, temperature T and pressure P. The enthalpy of the closed system is a function of state, H(T,P). When the closed system receives energy in a constant-pressure process, define the *constant-pressure thermal capacity* by

$C_P = \partial H(T,P)/\partial T$.

The constant-pressure thermal capacity is a function of state, $C_P(T,P)$—a property of the closed system.

Exercise. Show that $\partial S(T,P)/\partial T = C_P/T$.

Theory of ideal gas

The ideal gas law, $PV = Nk_BT$, was discovered empirically over centuries, before the discovery of entropy. Wiki the empirical discovery of the ideal gas law.

After the discovery of entropy, the ideal gas law is derived from a simple model, in just a few lines. This derivation makes the physical origin of the ideal gas law transparent.

Model an ideal gas as a closed system

A piston-cylinder setup contains N molecules. The molecules are called an *ideal gas* if they are far apart on average. The molecules fly, collide, and separate. For the time being, let all molecules be of the same species.

The piston-cylinder setup is a closed system. Recall the theory of closed system. Let U be the energy and V be the volume of the gas. When U, V, N are fixed, the gas is an isolated system. Denote the number of quantum states of this isolated system by Ω(U,V,N). Define the entropy of this isolated system by $S(U,V,N) = k_B \log \Omega(U,V,N)$. Recall that

$1/T = \partial S(U,V,N)/\partial U$,
$P/T = \partial S(U,V,N)/\partial V$.

These equations define functions $T(U,V,N)$ and $P(U,V,N)$. Invert the function $T(U,V,N)$, we obtain the function $U(T,V,N)$. When V and N are fixed, the gas is a thermal system. Define the thermal capacity under constant volume by

$C_V = \partial U(T,V,N)/\partial T$.

When the pressure P of the gas is fixed by a weight placed above the piston, the composite of the gas and the weight constitutes a thermal system. The energy of the thermal system is

$H = U + PV$.

The quantity is a property of the closed system, called the enthalpy of the closed system. Define the thermal capacity under constant volume by

$C_P = \partial H(T,P,N)/\partial T$.

Ideal gas law derived

Because the molecules are far apart, each molecule can fly anywhere in the volume V as if all other molecules are not there. Consequently, the number of quantum states of each molecule is proportional to V, and the number of quantum states of N molecules is proportional to V^N. The proportional factor depends on U and N, but not on V:

$\Omega(U,V,N) = V^N f(U,N)$,

where $f(U,N)$ is a function of U and N, but not V.

The entropy of the gas, $S = k_B \log \Omega$, is

$S(U,V,N) = Nk_B \log V + k_B \log f(U,N)$.

Inserting this expression into $P/T = \partial S(U,V,N)/\partial V$, we obtain that

$PV = Nk_BT$.

This equation of state is the ideal gas law.

Energy of an ideal gas

Inserting the expression for entropy into the definition of temperature, $1/T = \partial S(U,V,N)/\partial U$, we obtain that

$1/T = \partial(\log f(U,N))/\partial U$.

This equation shows that T is a function of U and N, and is independent of V. We invert the function $T(U,N)$ to $U(T,N)$. The energy is an extensive property, linear in the number of molecules N. Write

$U = Nu(T)$.

Here $u(T)$ is the energy per molecule.

Recall the definition of the thermal capacity per molecule under constant volume for a closed system, $c_V = \partial u(T,V)/\partial T$. For an ideal gas, we obtain that

$c_V(T) = du(T)/dT$,
$dU = Nc_V(T)dT$.

Enthalpy of an ideal gas

Recall the definition of enthalpy of a closed system, $H = U + PV$. For an ideal gas, $PV = Nk_BT$, so that $H = N(u + k_BT)$. The enthalpy per molecule is

$h(T) = u(T) + k_BT$.

Recall the definition of the thermal capacity per molecule under the condition of constant pressure for a closed system, $c_P = \partial h(T,P)/\partial T$. For an ideal gas, we obtain that

$c_P(T) = c_V(T) + k_B$,
$dH = Nc_P(T)dT$.

The ideal gas tables list the function $h(T)$ for many species of molecules.

Entropy of an ideal gas

Recall the general equation for a closed system

$dS = (1/T)dU + (P/T)dV$.

Inserting the equations specific to an ideal gas, $dU = Nc_V(T)dT$ and $PV = Nk_BT$, we obtain that

$dS = (Nc_P(T)/T)dT - (Nk_B/P)dP$.

We have used the relation $c_P = c_V + k_B$.

Entropy is a function of state. A state of the closed system is specified by two independent variables, T and P. In the above equation, the first term is due to the change in temperature, and the second term is due to the change in pressure.

Let T_0 be a reference pressure and P_0 be a reference pressure. Assume that we know the absolute entropy at this reference state, $S(T_0, P_0)$. Given the function $c_P(T)$, an integration gives that

$S(T, P) = Ns(T, P_0) - Nk_B \log (P/P_0)$.

The ideal gas tables list the absolute entropy per molecule, $s(T, P_0)$, as a function of T for many species of molecules.

Exercise. Assume a constant thermal capacity for an ideal gas. Calculate the function S(U,V).

Exercise. Use the ideal gas tables to find the energy, enthalpy, and entropy of O_2 at 1000 K, 1 MPa.

Exercise. Use the ideal gas tables to find the energy, enthalpy, and entropy of H_2O at 1000 K, 100 kPa.

Entropic elasticity

When a spring made of steel is pulled by a force, the spring elongates. When the force is removed, the spring recovers its initial length. This elasticity is due to a distortion of the electron cloud of atoms. Such elasticity is called *energetic elasticity*.

A bag of air acts like a spring. The volume decreases when the pressure increases, and recovers when the pressure drops. This elasticity clearly does not result from distortion of atomic bonds in the molecules, but from the change of the number of quantum states with volume. Such elasticity is called *entropic elasticity*.

Define *elastic modulus* by

$B = - V\partial P/\partial V$.

This definition is incomplete; we need to specify what is taken to be constant when we take the partial derivative. Let us consider two examples.

Isothermal elastic modulus. Under the isothermal condition, temperature is constant. Recall the ideal gas law, $P = NkT/V$. Taking the partial derivative, we obtain the isothermal elastic modulus

$B_T = P$.

Adiabatic elastic modulus. Assume constant thermal capacities, and let $k = c_P/c_V$. Under the adiabatic condition, PV^k= constant. Taking the partial derivative, we obtain the adiabatic elastic modulus

$B_{ad} = kP$.

A gas is stiffer under the adiabatic condition than under the isothermal condition.

Theory of osmosis

Osmosis. Consider N particles dispersed in a bag of water of volume V. The particles are different from water molecules, and can be of any size. The particles can be of many species. When the particles are molecules, we call them *solutes*. When the particles are somewhat larger, say from 10 nm to 10 μ m, we call them *colloids*. The bag is immersed in a tank of pure water. The bag is made of a semipermeable membrane: water can permeate through the membrane but the particles cannot.

Osmotic pressure. The physics of this situation is analogous to the ideal gas, provided that the concentration of the particles is dilute. Every particle is free to explore the entire volume in the bag. The number of quantum states of the water-particle system scales as

$\Omega \propto V^N$.

As water permeates through the membrane, the volume of the bag V changes.

Recall $S = k_B \log\Omega$ and the $P/T = \partial S(U,V)/\partial V$, we obtain that

$P = k_B TN/V$.

This pressure is called the *osmotic pressure*. The ratio N/V is called the *concentration* of solute. The law of osmosis is identical to the law of ideal gas.

Balance osmotic pressure by tension. The osmotic pressure can be balanced in several ways. For example, the tension in the membrane can balance the osmosis pressure. One can also disperse particles in the tank of water outside the bag. The difference in the concentration of particles in the bag and that of particles in the tank causes a difference in the pressures in the bag and in the tank. The difference in pressure can be balanced by the tension in the membrane. Youtube osmosis (dialysis bag).

Balance osmotic pressure by gravity. As yet another example, we place a rigid, semi-permeable wall in the liquid, with the particles on one side, but not the other. Water is on both sides of the wall, but alcohol is only on one side. The molecules of the liquid can diffuse across the wall, but the particles cannot. For the particles to explore more volume, the liquid molecules have to diffuse into the side where particles are. If this experiment were carried out in the zero-gravity environment, the infusion would continue until the pure liquid is depleted. In the gravitational field, however, the infusion stops when the pressure in the solution balances the tendency of the infusion. Youtube osmosis (U-tube).

Nobel Lecture. van't Hoff, Osmotic pressure and chemical equilibrium, 1901.

BAT on pure substance

A fixed amount of a pure substance is a closed system. Its thermodynamic states are specified by two independent properties. For now, we choose the two independent properties to be energy U and volume V. Once U and V are fixed, a fixed amount of the pure substance becomes an isolated system. This model neglects many effects, such as gravitational field, elastic field, electrical field, and magnetic field.

The isolated system has a certain number of quantum states. Denote the number of quantum states by $\Omega(U,V)$, and write $S(U,V) = \log \Omega(U,V)$. Recall the identity $dS = (1/T)dU + (P/T)dV$.

Primitive surfaces

We now describe the thermodynamic theory of phases of a pure substance due to Gibbs (A method of geometric representation of the thermodynamic properties by means of surfaces, 1873). Before Gibbs developed this theory, the empirical facts of pure substances described above were known. They were so numerous and called for a theory.

Energy, volume, and entropy are extensive properties. Let u, v, and s be the energy, volume, and entropy of the substance per molecule. The variables u, v, s form the axes of a three-dimensional space.

For the time being, let us represent each phase by its own energy-volume-entropy relation, s(u,v), corresponding to a surface in the energy-volume-entropy space. The three phases correspond to three surfaces. Gibbs called them the *primitive surfaces*. A point on one of the three primitive surfaces corresponds to a homogeneous state of the substance.

Rule of mixture

Consider two homogeneous states, A and B, which can be two points either on one primitive surface, or on two primitive surfaces. A mixture of the two homogeneous states has a total of N molecules, of which N_A molecules are homogeneous state A, and N_B molecules are in homogeneous state B. Denote the number fractions of the molecules by $y_A = N_A/N$ and $y_B = N_B/N$. The total number of molecules in the mixture is conserved:

$N = N_A + N_B$.

Divide this equation by N, and we obtain that

$y_A + y_B = 1$.

Both y_A and y_B are non-negative numbers.

Denote the energies, volumes, and entropies of the two homogeneous states by (u_A,v_A,s_A) and (u_B,v_B,s_B). Let u, v, and s be the energy, volume, and energy of the mixture divided by the total number of molecules. Energy is an extensive variable, so that the energy of the mixture is the sum of the energies of the two homogeneous states:

$Nu = N_Au_A + N_Bu_B$.

Divide this equation by N, and we obtain that

$u = y_Au_A + y_Bu_B$.

The same rule applies to volume and entropy:

$v = y_Av_A + y_Bv_B$,
$s = y_As_A + y_Bs_B$.

The rules of mixture have a graphic interpretation in the energy-volume-entropy space. The two homogeneous states, (u_A,v_A,s_A) and (u_B,v_B,s_B), are two points on one or two primitive surfaces. The mixture, (u,v,s), is a point on the line joining the two points (u_A,v_A,s_A) and (u_B,v_B,s_B), located at the center of gravity, depending on the fraction of molecules y_A and y_B allocated to the two homogeneous states. In general, the mixture (u,v,s) is a point off the primitive surfaces.

We can generalize the rules of mixture to a mixture of three homogeneous states. A pure substance has a total of N molecules, of which N_A, N_B, and N_C molecules are in the three homogeneous states. Denote the number fractions by $y_A = N_A/N$, $y_B = N_B/N$, and $y_C = N_C/N$. Here $y_{A,}$ y_B and y_C are non-negative numbers. The mixture conserves the number of molecules:

$N_A + N_B + N_C = N$.

Divide this equation by N, and we obtain that

$y_A + y_B + y_C = 1$.

The three homogeneous states, (u_A,v_A,s_A), (u_B,v_B,s_B), and (u_C,v_C,s_C), are three points on one or two primitive curves. The three points form a triangle in the energy-volume-entropy space. The energy, volume, and entropy per molecule of the mixture (u,v,s) are given by

$u = y_A u_A + y_B u_B + y_C u_C$,
$v = y_A v_A + y_B v_B + y_C v_C$,
$s = y_A s_A + y_B s_B + y_C s_C$.

The mixture, (u,v,s), is a point in the energy-volume-entropy space, located at the center of gravity in the triangle, depending on the fraction of molecules $y_{A,}$ y_B and y_C allocated to the three homogeneous states at the vertices of the triangle. In general, the mixture (u,v,s) is a point off the primitive surfaces.

We can further generalize the rules of mixture to a mixture of any number of homogenous states. Now consider all possible mixtures of arbitrary numbers of homogeneous states. Given the primitive surfaces, the rules of mixture create a set of points, which constitute a solid figure in the energy-volume-entropy space. In general, each point in the solid figure represents a mixture.

In the language of convex analysis, the energy-volume-entropy space is called a vector space, and each point in the vector space is called a vector. All the homogeneous states on the primitive surfaces form a set of vectors. A mixture is called a *convex combination* of the homogenous states. The set of all mixtures is called the *convex hull* of homogenous states. Wiki convex combination. Wiki convex hull.

Derived surface

Gibbs called the upper-bound surface of all mixtures the *derived surface*. This surface is derived by rolling a plane tangent to the primitive surfaces. In the energy-volume-entropy space, a tangent plane can touch the primitive surfaces at one, two, or three points, but not four or more points.

When a tangent plane touches the three primitive surfaces at three points, the three tangent points are the vertex of a triangle.

From each edge of the triangle we roll out the tangent plane to touch two primitive surfaces at two points. The two tangent points are the ends of a straight-line segment, called the tie line.

From each vertex of the triangle, we retain a convex part of a primitive surface. The derived surface has a single sheet, and is a *convex surface*.

So far, the three quantities—energy, volume, and entropy—play similar roles. All we have invoked is that they are extensive quantities. We next isolate a fixed amount of a pure substance by fixing energy and volume. This isolated system has an enormous number of internal variables: the number of homogeneous states, the location of each homogeneous state on a primitive surface, and the number fraction of molecules allocated to each homogeneous state.

When a fixed amount of a substance is isolated with a fixed energy u and a fixed volume v, the substance in general is a mixture, corresponding to a point on a vertical line. Such a mixture in general is *not* in equilibrium. The isolated system reaches equilibrium when the subset entropy maximizes—that is, when the vertical intersects the derived surface.

Thus, every point on the derived surface corresponds to a state of equilibrium. We next list distinct types of equilibrium.

Equilibrium of a single homogeneous state

If a plane tangent to one point on a primitive surface does not cut any primitive surfaces, this point of the primitive surface belongs to the derived surface. The point corresponds to a single homogenous state in equilibrium. Gibbs called the set of all such points the *surface of absolute stability*. The tangent plane can roll on the primitive surface to change the two slopes of the tangent plane independently. The slopes of the tangent plane determines the temperature and pressure of the state. Thus, the surface of absolute stability has two degrees of freedom.

Equilibrium of two homogeneous states

If a plane tangent to two points on the primitive surfaces does not cut any primitive surfaces, the straight-line segment connecting the two tangent points belongs to the derived surface. The straight-line segment is called a *tie line*. The common tangent plane can roll on the two primitive surfaces to change its slope by a single degree of freedom. As the common tangent plane rolls, the tie lines form a developable surface, and the two tangent points trace out two curves on the primitive surfaces. Gibbs called the two curves the *limits of absolute stability*.

Equilibrium of three homogeneous states

If a plane tangent to three points on the primitive surfaces and does not cut any primitive surfaces, the triangle connecting these three points belongs to the derived surface. The tangent plane has no degree of freedom to roll, and is fixed in the energy-volume-entropy space.

Equilibrium of four homogeneous states is impossible for a pure substance

A pure substance can have more than three phases. For example, H_2O molecules can form many crystalline structures at high pressure. Each crystalline structure corresponds to a distinct phase. Can four or more homogeneous states equilibrate? The answer is no, so long as the states of the pure substance are specified by two independent variables.

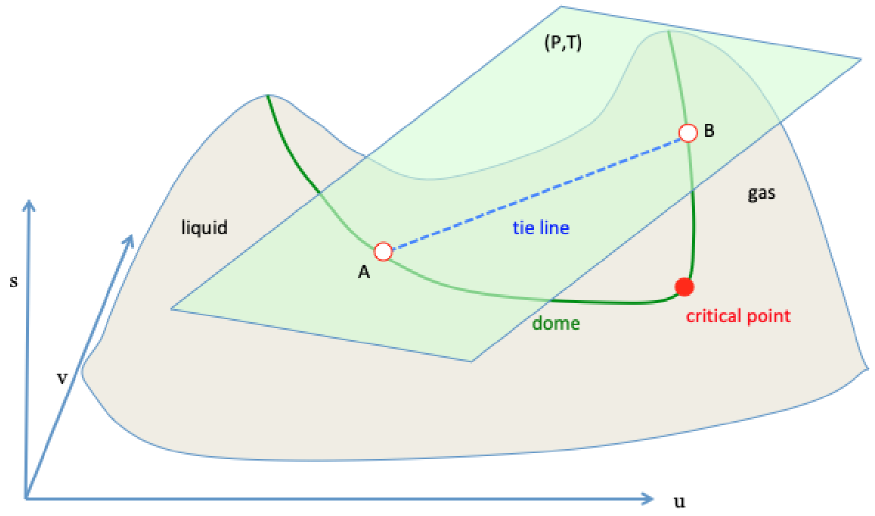
In the two-variable model, each phase corresponds in the entropy-volume-energy space to a surface—a primitive surface. Four phases correspond to four primitive surfaces. A plane rolling over the four primitive surfaces can at once touch one primitive surface, two primitive surfaces, or three primitive surfaces, but not four primitive surfaces. The exception is that all four primitive surfaces are exactly positioned to have a common tangent plane. The chance for such an exception is negligible.

Critical state

Gibbs (1873) introduced the theory of critical state. He cited a paper by Andrews (1869), which reported the experimental observation of a substance changing from a liquid state to a gaseous state without crossing any states of two-phase coexistence. Gibbs wrote:

"...the derived surface which represents a compound of liquid and vapor is terminated as follows: as the tangent plane rolls upon the primitive surface, the two points of contact approach one another and finally fall together. The rolling of the double tangent plane necessarily come to an end. the point where the two points of contact fall together is the critical state."

Gibbs modeled a pure substance with two primitive surfaces: a convex surface for the solid phase, and a nonconvex surface for the liquid and gas phases. Google Books: Scientific Papers of J. Willard Gibbs



Exercise. YouTube Gibbs surface and Maxwell cast.

A. In the energy-volume-entropy space, sketch the primitive water-steam surface. Describe the surface with words.
B. Sketch the derived water-steam surface. Describe the surface with words.
C. Derive equations that determine a tie line.

Metastability

A primitive surface may contain a convex part and a non-convex part. The curve separating the two parts is called the limit of metastability. If a convex part of the primitive surface lies below a tangent plane of the derived surface, the part of the primitive surface is beyond the limit of absolute stability. Each point of this part of the primitive surface is called a metastable state. Gibbs noted that such a state is stable in regard to continuous changes of state, but is unstable in regard to discontinuous changes of state.

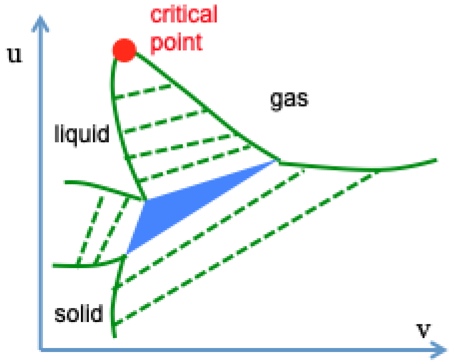
Energy-volume plane

Gibbs projected the derived surface onto the volume-entropy plane. He drew the triangle for the states of coexistence three phases, limits of absolute stability, limits of metastability, and critical state. He did not, however, draw the primitive surfaces and the derived surface in the energy-volume-entropy space.

Maxwell drew the surface in the energy-volume-entropy space in a later edition of his textbook, *Theory of Heat*.

Planck projected the derived surface on the energy-volume plane (Figure 4) in his textbook, *Treatise on Thermodynamics*. Planck made a mistake of adding a critical state for the solid-liquid transition. Such a critical state does not exist.

Here I sketch the projection of the derived surface to the energy-volume plane. Both energy and volume are extensive quantities, so that each thermodynamic state corresponds to a distinct point in the energy-volume plane.



Exercise. Find the data to draw the ice-water-steam triangle on the energy-volume plane.

Exercise. Find the data to draw the water-steam dome on the energy-entropy plane. Include the critical point, several tie lines in the dome. Also include the ice-water-steam triangle, the ice-steam belt, and ice-water belt.

Temperature and pressure

In the above, we have developed the entire theory using only three functions of state: energy, volume, and entropy. Each is an extensive property, and obeys the rule of mixture. We next discuss the roles of the other two functions of state: temperature and pressure, which are intensive properties.

Write the derived surface as a function s(u,v). Recall the meanings for the slopes of the surface s(u,v):

$1/T = \partial s(u,v)/\partial u$,
$P/T = \partial s(u,v)/\partial v$.

When the substance equilibrates in a mixture of two homogeneous states, a tangent plane contacts the primitive surfaces at two points, (u_A,v_A,s_A) and (u_B,v_B,s_B). The tangent plane has the same slopes at the two points, so that the two homogeneous states have the same temperature and pressure:

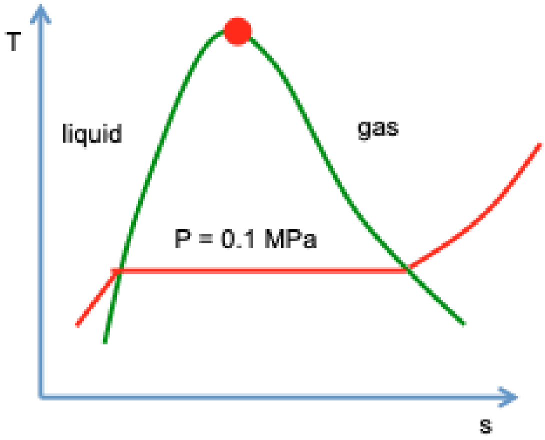
$1/T = \partial s_A(u_A,v_A)/\partial u_A = \partial s_B(u_B,v_B)/\partial u_B$,
$P/T = \partial s_A(u_A,v_A)/\partial v_A = \partial s_B(u_B,v_B)/\partial v_B$.

The tangent plane cuts the vertical axis of entropy at some point. The intercept can be calculated using the quantities at either the state (u_A,v_A,s_A) or the state (u_B,v_B,s_B), so that

s_A - (1/T)u_A - (P/T)v_A = s_B - (1/T)u_B - (P/T)v_B.

The above equations transcribe the geometrical expressions of the condition of equilibrium into analytical expressions. Once the characteristic functions of the two phases are given, s_A(u_A,v_A) and s_B(u_B,v_B), for a given temperature, the above equations solve the pressure P and the two tangent points (u_A,v_A,s_A) or the state (u_B,v_B,s_B).

Temperature-entropy plane.



Exercise. For a unit mass of water molecules, a thermodynamic state is specified by two of thermodynamic properties among many, such as temperature T, pressure P, specific energy u, specific volume v, specific entropy s, specific enthalpy h, and quality x. For each of the thermodynamic states specified below, use the steam tables to determine the other thermodynamic properties.
(a) T = 100 Celsius, x = 0.9.
(b) T = 100 Celsius, P = 10 kPa.
(c) T = 100 Celsius, P = 500 kPa.
(d) T = 50 Celsius, v = 1 m^3/kg.

Exercise. We have described the conditions of the equilibrium of three homogeneous states in geometric terms. Transcribe these conditions in equations.

Exercise. YouTube Gibbs surface and Maxwell cast.

A. In the energy-volume-entropy space, sketch the primitive water-steam surface. Describe the surface with words.
B. Sketch the derived water-steam surface. Describe the surface with words.
C. Derive equations that determine a tie line.

Alternative independent properties

Entropy S(U,V)

Properties. A state of a closed system is specified by prescribing values of two independent properties. All other properties are functions of the two independent properties. We have met many properties, including the five leading properties: S, U, V, P, and T. Any two of the properties can serve as independent properties to specify the states of the closed system.

We next look at few alternative choices of independent properties, and relate these choices to experiments.

U and V as independent properties. Of the five leading properties, so far energy U and volume V have served as independent properties. The other three properties are functions of the independent properties, S(U,V), T(U,V), and P(U,V).

When U and V are fixed, the closed system becomes an isolated system. Denote the number of quantum states of the isolated system by Ω(U,V). Define $S(U,V) = k_B \log \Omega(U,V)$ the entropy of the isolated system.

Recall that S, U, V are extensive properties, so that the (S, U, V) space is a three-dimensional vector space. In the (S, U, V) space, the function S(U,V) is a surface.

Recall a fact in calculus. For a function S(U,V), when the independent variables change by dU and dV, the function changes by

$dS(U,V) = (\partial S(U,V)/\partial U)dU + (\partial S(U,V)/\partial V)dV.$

The two partial derivatives are the slopes of a plane tangent to the surface S(U,V) at point (S, U, V).

The two slopes of the tangent plane determines two other functions of state—temperature T(U,V) and pressure P(U,V):

$1/T = \partial S(U,V)/\partial U,$
$P/T = \partial S(U,V)/\partial V.$

Thus, the other two functions of state, T(U,V) and P(U,V), are deduced from the function of state, S(U,V). We call the latter a *characteristic function* of a closed system.

The above two relations, along with the fact in calculus, imply an equation of a closed system:

$dS = (1/T)dU + (P/T)dV$.

We next consider other choices of independent properties, which lead to alternative characteristic functions. The change of independent properties may bring some convenience, but adds no new information.

Exercise. Is P(U,V) a characteristic function of a closed system?

Exercise. Assume that an ideal gas has a constant thermal capacity per molecule, c_V. Determine the characteristic function s(u,v).

Energy U(S,V)

S and V as independent properties. Recall that S(U,V) is an increasing function of U. We can invert this function to obtain the function U(S,V).

This inversion is purely mathematical, and adds or loses no information. Both functions S(U,V) and U(S,V) characterize the same closed system, and correspond to the same surface in the energy-volume-entropy space.

Rearrange the equation $dS = (1/T)dU + (P/T)dV$ as

$dU = TdS - PdV$.

This equation interprets the partial derivatives of the function U(S,V):

$T = \partial U(S,V)/\partial S, \quad -P = \partial U(S,V)/\partial V$.

These relations express the other two functions of state, T(S,V) and P(S,V), in terms of the function of state U(S,V). Thus, U(S,V) is a characteristic function of a closed system.

Caution. The function U(S,V) was introduced by Gibbs (1873), and he used it in much of his subsequent work. But this function puts entropy in a position similar to volume, and is unsuitable for learning fundamentals of entropy.

Work and heat in a reversible process. Recall the definition of the energy transfer by heat:

$dQ = dU + dW$.

In a reversible process, the energy transfer by work from the closed system to its surroundings is

$dW = PdV$,

and the energy transfer by heat from the surroundings to the closed system is

$dQ = TdS$.

Thermal capacity of a closed system in a constant-volume process. Recall the definition of thermal capacity:

$C = \partial Q/\partial T$.

For a closed system, Q is not a function of state, but depends on process. Consider a constant-volume process. When the piston in the cylinder-piston setup is jammed, the closed system becomes a thermal system, so that $dW = 0$ and $dQ = dU$. Denote the thermal capacity in the constant-volume process by

$C_V = \partial U(T,V)/\partial T$.

Though defined by a process, C_V is a function of state, $C_V(T,V)$.

Exercise. Is U(T,V) a characteristic function of a closed system?

Enthalpy H(S,P)

Once again consider a closed system, such as a half cylinder of water in a cylinder-piston setup. A weight is placed above the piston, and a fire is is in thermal contact with the water.

A closed system and a weight together constitute a thermal system

Let P be the pressure inside the cylinder, and A be the base area of the piston. The piston moves without friction. The pressure in the cylinder pushes the piston up. The balance of forces requires that the weight above the piston should be PA. When the weight is constant, the pressure inside the cylinder is also constant.

When the weight is at a height z, the volume of the cylinder is $V = Az$, and the potential energy of the constant weight is $PAz = PV$. The water and the weight together constitute a thermal system. The internal energy of the composite is the sum of the internal energy of the water molecules in the cylinder, U, and the potential energy of the weight, PV. Denote the internal energy of this thermal system by

$H = U + PV$.

Even though we constructed H using a composite, H relates to U, P, V, which are properties of the closed system. Consequently, H is also a property of the closed system. The quantity H is called the *enthalpy* of the closed system. Enthalpy was introduced by Gibbs (1875).

Thus, the same experimental setup can be viewed as a closed system or a thermal system, depending on how we partition parts of the setup into a system and its surroundings.

H(S,P) is a characteristic function of a closed system

Recall the product rule in calculus, and we obtain that

$dH = dU + PdV + VdP$.

Combining with $dS = (1/T)dU + (P/T)dV$, we obtain that

$dH = TdS + VdP$.

We regard the enthalpy as a function of entropy and pressure, H(S,P). The above equation interprets the partial derivatives:

$T = \partial H(S,P)/\partial S$, $V = \partial H(S,P)/\partial P$.

These equations express the two functions of state, T(S,P) and H(S,P), in terms of the function H(S,P). Thus, H(S,P) is a characteristic function of a closed system.

Thermal capacity of a closed system in a constant-pressure process

Enthalpy is used to measure energy transfer by heat to the closed system in a constant-pressure process. When the pressure of a closed system system is fixed by a constant weight, the closed system and the weight together constitute a thermal system. The Internal energy of the thermal system is the sum, $H = U + PV$. Denote the thermal capacity of the thermal system by

$C_P = \partial H(T,P)/\partial T$.

Though defined by a process, C_P is a function of state, $C_P(T,P)$. It is the thermal capacity of the closed system in a constant-pressure process.

Exercise. Is H(T,P) a characteristic function of a closed system?

Helmholtz function F(T,V)

Define the Helmholtz function by

$F = U - TS$.

This function was introduced by Gibbs (1875), and is called the *Helmholtz function*, or *Helmholtz free energy*.

The energy U has an arbitrary additive constant, which also appears in F. The Helmholtz function is an extensive quantity, and is a function of state of the closed system.

Let us do some calculus on the Helmholtz function first, and then relate the Helmholtz function to experiments.

Helmholtz function F(T,V) is a characteristic function of a closed system

Note that

$dF = dU - TdS - SdT$.

This equation, together with the equation $dS = (1/T)dU + (P/T)dV$, gives

$dF = -SdT - PdV$.

This equation suggests that the Helmholtz function of the closed system should be a function of temperature and volume, F(T,V).

Recall a fact in calculus. For any function F(T,V), when the independent variables change by dT and dV, the function changes by

$dF = (\partial F(T,V)/\partial T)dT + (\partial F(T,V)/\partial V)dV$.

A comparison of the above two equations indicate that

$-S = \partial F(T,V)/\partial T, \quad -P = \partial F(T,V)/\partial V$.

These equations express two functions state, S(T,V) and P(T,V), in terms of the Helmholtz function F(T,V). Recall the definition of the Helmholtz function, $F = U - TS$. This equation determines the function U(T,V).

Thus, we can choose T and V as independent properties, characterize a closed system by the Helmholtz function F(T,V), and express functions S(T,V), P(T,V), and U(T,V) in terms of the Helmholtz function. Thus, F(T,V) is a characteristic function of a closed system.

Recall the definition of the constant-volume thermal capacity:

$C_V = \partial U(T,V)/\partial T$.

The subscript V indicates that the volume is fixed. This definition interpretes one partial derivative of the function U(T,V).

Maxwell relation

Recall a fact in calculus:

$\partial(\partial F(T,V)/\partial T)/\partial V = \partial(\partial F(T,V)/\partial V)/\partial T$.

We obtain that

$\partial S(T,V)/\partial V = \partial P(T,V)/\partial T$.

This equation is called a Maxwell relation.

Increment of the function U(T,V)

Start with an identity in calculus:

$dU = (\partial U(T,V)/\partial T)dT + (\partial U(T,V)/\partial V)dV$.

Recall $dU = TdS - PdV$. Now we regard T and V as independent variable, so that

$\partial U(T,V)/\partial V = T\partial S(T,V)/\partial V - P$

Using a Maxwell relation, $\partial S(T,V)/\partial V = \partial P(T,V)/\partial T$, we change the above equation to

$\partial U(T,V)/\partial V = T\partial P(T,V)/\partial T - P$

Now we have both partial derivatives of the function U(T,V), so that

$dU = C_V(T,V)dT + (T\partial P(T,V)/\partial T - P)dV$.

This equation relates dU to two functions $C_V(T,V)$ and P(T,V).

Increment of the function S(T,V)

Recall the equation $dS = (1/T)dU + (P/T)dV$, Inserting the above expression for dU, we obtain that

$dS = (C_V(T,V)/T)dT + (\partial P(T,V)/\partial T)dV$.

This relation indicates that we can determine the function S(T,V) by measuring the two functions $C_V(T,V)$ and P(T,V).

BAT on a closed system in a constant-volume, constant-temperature process

Enough about calculus. Let us relate the Helmholtz function to experiments. To fix the volume of the closed system, we jam the piston, so the closed system becomes a thermal system. To fix the temperature of a closed system, we place the closed system in thermal contact with a thermal reservoir of constant temperature T. We next run the BAT on a constant-pressure process, constant-temperature.

Step 1. construct an isolated system with internal variables. The composite of the closed system and the thermal reservoir is an isolated system with two internal variables: the internal energy of the closed system, U, and the internal variable of the closed system, x.

The energy of the isolated system, $U_{composite}$, is the sum of the energy of the closed system, U, and the energy of the thermal reservoir, U_R. That is,

$U_{composite} = U + U_R$.

The isolated system conserves energy, so that $U_{composite}$ is constant as the closed system changes state.

Step 2. Determine the subset entropy of the isolated system as a function of the two internal variables. The isolated system—the composite of the closed system and the thermal reservoir—is characterized by the subset function S(U,V,x). The thermal reservoir is a thermal system of constant temperature T, characterized by a function $S_R(U_R)$. Because T is fixed, the function is linear in U_R:

$S_R(U_R) = S_R(U_{composite}) + (U_R - U_{composite})/T$.

The subset entropy of the isolated system is

$S_{composite}(U, V, x) = S(U,V,x) + S_R(U_{composite}) - U/T$.

Step 3. Maximize the subset entropy to reach equilibrium. The composite isolated for a long time reaches equilibrium. When the isolated system is in thermal equilibrium, recall a fact in calculus:

$\partial S_{composite}/\partial U = 0$.

When temperature T is constant, the above equation recovers the familiar condition:

$1/T = \partial S(U,V, x)/\partial U$.

Given the function S(U,V, x), this equation solves the function U(T,V,x). We can also write the entropy of the closed system as a function S(T,V,x).

Thus, x is the only remaining internal variable of the isolated system. The basic algorithm requires x to change to increase $S_{composite}$, or equivalently, to increase the function

$J = S - U/T$.

The term S is the entropy of the closed system, and the term - U/T is the reduction of the entropy of the reservoir when the reserve transfers energy U to the closed system.

The function J(T,V,x) is called the *Massieu function*, or the *Massieu free entropy*.

In maximizing the function J(T,V,x), T and V are fixed, and only x is variable. Aside from additive constants, the function J(T,V,x) is the subset entropy of an isolated system: the composite of a closed system of a fixed volume V, and a thermal reservoir of a fixed temperature T.

Algorithm of thermodynamics for a constant-volume, constant-temperature process

We now paraphrase the basic algorithm of thermodynamics for a constant-volume and constant-temperature process.

1. Construct a closed system with a fixed volume V and an internal variable x.
2. Fund the function J(T,V,x) = S - U/T.
3. *Equilibrium*. Find the value of the internal variable x that maximizes the function J(T,V,x). In this maximization, T and V are constant, and x is variable.
4. *Irreversibility*. Change the value of the internal variable x in a sequence that increases the function J(T,V,x).

Note that $F = - TJ$ is the Helmholtz function. Because T is fixed, maximizing $J(T,V,x)$ is equivalent to minimizing $F(T,V,x)$. The above algorithm can be paraphrased in terms of minimizing $F(T,V,x)$.

Gibbs function G(T,P)

The half cylinder of water and the weight above the piston together constitute a thermal system of energy $U + PV$. The Helmholtz function of this thermal system is

$$G = U + PV - TS.$$

This quantity was introduced by Gibbs (1875), and is called the Gibbs function, or the Gibbs free energy.

The energy U has an arbitrary additive constant, which also appears in G. The Gibbs function is an extensive quantity, and is a function of state.

Gibbs function G(T,P) is a characteristic function of a closed system

Note that

$$dG = dU + PdV + VdP - TdS - SdT.$$

Recall that $dS = (1/T)dU + (P/T)dV$, and we obtain that

$$dG = - SdT + VdP.$$

We regard the Gibbs function as a function of pressure and temperature, $G(T,P)$. The above equation interprets the partial derivatives:

$$-S = \partial G(T,P)/\partial T, \quad V = \partial G(T,P)/\partial P.$$

These equations express two functions state, $S(T,P)$ and $V(T,P)$, in terms of the Gibbs function $G(T,P)$.

Recall the definition of the Gibbs function, $G = U + PV - TS$, and the definition of the enthalpy, $H = U + PV$. These definitions gives that

$$H(T,P) = G + TS = G(T,P) - T\partial G(T,P)/\partial T.$$

This equation expresses the function H(T,P) in terms of the Gibbs function G(T,P).

In summary, once the Gibbs function G(T,P) is known, we can calculate all the other functions of state. Thus, G(T,P) is a characteristic function of a closed system.

Other mathematical relations

Here is a Maxwell relation:

$-\partial S(T,P)/\partial P = \partial V(T,P)/\partial T.$

Exercise. Derive this Maxwell equation.

Recall the definition of the thermal capacity of a closed system in a constant-volume process, $C_P = \partial H(T,P)/\partial T$. We obtain that

$dH = C_P(T,P)dT + (V - T\partial V(T,P)/\partial T)dP,$
$dS = (C_P(T,P)/T)dT - (\partial V(T,P)/\partial T)dP.$

Exercise. Derive the above two equations.

BAT on a closed system in a constant-pressure, constant-temperature process

Step 1. Construct an isolated system with internal variables. Consider a closed system with an internal variable x. For example, the closed system can be a half cylinder of water sealed by a frictionless piston, and the internal variable can be the number of H_2O molecules in the vapor inside the cylinder.

The molecules in the cylinder are in mechanical equilibrium with a fixed weight above the piston. By the balance of forces, the weight relates to the pressure inside the cylinder as PA, where A is the base area of the piston. The water molecules are in thermal equilibrium with a thermal reservoir of constant temperature T. We identify the composite of the water molecules, the weight, and the thermal reservoir as an isolated system with three internal variables: the internal energy of the water molecules U, the volume enclosed by the cylinder V, and x.

The energy of the isolated system is

$U_{composite} = U + PV + U_R.$

Here U is the internal energy of the water molecules, PV is the potential energy of the weight, and U_R is the internal energy of the thermal reservoir. The isolated system conserves energy, so that $U_{composite}$ = constant.

Step 2. Find the subset entropy of the isolated system as a function of internal variables. The water molecules constitute a closed system, characterized by a function $S(U,V,x)$. The entropy of the weight S_{weight} is constant. The thermal reservoir reservoir is a thermal system of constant temperature T, characterized by a function $S_R(U_R)$, so that $S_R(U_R) = S_R(U_{composite}) + (U_R - U_{composite})/T$.

The subset entropy of the composite is the sum of the parts:

$$S_{composite} = S(U,V,x) + S_{weight} + S_R(U_{composite}) - (U + PV)/T.$$

Step 3. Maximize the subset entropy to reach equilibrium. The isolated system is in thermal and mechanical equilibrium, so that

$$\partial S_{composite}/\partial U = 0 \text{ and } \partial S_{composite}/\partial V = 0.$$

When pressure P and temperature T are constant, the two conditions recover the familiar conditions:

$$1/T = \partial S(U,V, x)/\partial U \text{ and } P/T = \partial S(U,V, x)/\partial V.$$

Given the function $S(U,V, x)$, these two equations solve the function $U(T,P,x)$ and $V(T,P,x)$. We can also write the entropy as a function $S(T,P,x)$.

Step 4. Increase the subset entropy to see irreversibility. Thus, x is the only remaining internal variable. The basic algorithm requires x to change to increase $S_{composite}$, or equivalently, to increase the function

$$Y = S - (U + PV)/T.$$

This function is called the *Planck function*, or the *Planck free entropy.* In maximizing this function $Y(T,P,x)$, T is fixed by the thermal reservoir, P is fixed by the weight above the pistor, and only x is variable. Aside from additive constants, this function $Y(T,P,x)$ is the subset entropy of an isolated system: the composite of the closed system, the thermal reservoir, and the weight.

Algorithm of thermodynamics for a constant-pressure, constant-temperature process

We now paraphrase the basic algorithm of thermodynamics for a constant-pressure and constant-temperature process.

1. Construct a closed system with an internal variable x.
2. Find the function Y(T,P,x) = S - (U +PV)/T.
3. *Equilibrium*. Find the value of the internal variable x that maximizes the function Y(T,P,x). In this maximization, T and P are constant, and x is variable.
4. *Irreversibility*. Change the value of the internal variable x in a sequence that increases the function Y(T,P,x).

Note that G = -TY. Because T is fixed, maximizing Y(T,P,x) is equivalent to minimizing G(T,P,x). The above algorithm can be paraphrased in terms of minimizing the Gibbs function G(T,P,x).

Exercise. Use the Planck function to derive the equilibrium condition of two phases: $s_A - (1/T)u_A - (P/T)v_A = s_B - (1/T)u_B - (P/T)v_B$.

Free entropy vs free energy

We are all Gibbsians. Gibbs is timeless. Thermodynamics after him has remained unchanged in its aim and method, despite numerous applications. Today we use thermodynamics in the way as he taught us. Carnot and Clausius invented entropy, Boltzmann discovered what entropy is, and Gibbs made entropy useful.

Free entropy. Before Gibbs published his 1873 paper, Massieu (1869) discussed relations between functions of state, and showed that certain such relations are capable of generating all other thermodynamic relations.

Both the function J = S - U/T and the function Y = S - (U +PV)/T were introduced by Massieu (1869), and the function Y was extensively used later by Planck. We will call J the Massieu function, and Y the Planck function. The two functions are also called free entropies. Wiki free entropy.

S. Bordoni, Routes towards an abstract thermodynamics in the late nineteenth century. The European Physical Journal H 38, 617 (2013).

Let no shadow distract us from the real thing. People often say that they determine equilibrium by minimizing energy. This statement is confusing. Energy of an isolated system is conserved. To reach equilibrium, what we really do is to maximize the subset entropy of an isolated system. Thermodynamics has a single basic algorithm. We just learn to construct, for each given situation, an isolated system with internal variables.

When confused, isolate.

Gibbs (1875) cited Massieu's (1869) prior work on free entropy, and still thrusted upon us the two quantities: the Helmholtz function F(T,V) and the Gibbs function G(T,P). Gibbs did not tell us why he replaced J and Y with the equivalent functions F and G.

The free entropies J and Y keep us focused on the leading actor—entropy. They are the subset entropies of isolated systems of two types. Any application of thermodynamics requires us to identify an isolated system. The free energies F and G divert our attention to the supporting actor—energy. Like entropy, J and Y are dimensionless and appear in all equations naturally whenever F and G appear.

Of all laws of Nature, only the law of entropy expresses an inequality. Thermodynamics only maximizes one function: the subset entropy of an isolated system as a function of internal variables. The Helmholtz function and Gibbs function are shadows of entropy. Let no shadow distract us from the real thing—entropy.

Nature singles entropy out for all questions of equilibrium and irreversibility. In dealing systems under constant temperature and pressure, Gibbs should have followed Massieu (1869), and should not twist the logic from entropy to energy. The beginning sections of his 1875 paper are unreadable not because they contain profound thoughts, but because they twist ideas.

Exercise. Critique the following extract from Gibbs (1875).

"For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive."

Google book. The Collected Works of J. Willard Gibbs.

Exercise. Gibbs was perhaps needlessly enamored with energy. May this blemish of his great work annoy you, not repel you from reading his great work. To make sure that the blemish does annoy you, please paraphrase the algorithm of thermodynamics of constant pressure and constant temperature using "free volume", instead of free entropy or free energy. Someone enamored with space may wish to divert our attention from entropy to volume.

Equilibrium of two homogeneous states by equating the Gibbs function

Two homogeneous states in equilibrium have equal values of temperature T and pressure P, but have different values of energy, volume, and entropy per molecule.

The phase boundary between two phases of a pure substance has a single degree of freedom. We can regard T as the independent variable. Along the phase boundary, P, s_A, s_B, u_A, u_B, v_A, and v_B are functions of T.

Let the Gibbs function per molecule in homogeneous state A be

$g_A(T,P) = u_A + Pv_A - Ts_A$.

Let the Gibbs function per molecule in homogeneous state B be

$g_B(T,P) = u_B + Pv_B - Ts_B$.

The Gibbs function per molecule of a mixture of the two homogeneous states is

$g = y_A g_A(T,P) + y_B g_B(T,P)$.

The change of phase is modeled as a process of constant temperature and constant pressure. Recall that $y_A + y_B = 1$. The fraction of molecules in one homogenous state, y_A, is the independent internal variable, which is varied to minimize the Gibbs function of the mixture. The condition of equilibrium is

$g_A(T,P) = g_B(T,P)$

This equation is the same as

$u_A + Pv_A - Ts_A = u_B + Pv_B - Ts_B$.

This condition reproduces what we have obtained by maximizing entropy.

Clapeyron equation

Slope of a two-phase boundary. A two-phase boundary of a pure substance is a curve on the temperature-pressure plane. That is, the phase boundary is a function P(T).

At a point (T, P) on the phase boundary, the two phases have the equal value of the Gibbs function:

$g_A(T,P) = g_B(T,P)$.

At another point (T + dT, P + dP) on the phase boundary, the two phases also have the equal value of the Gibbs function:

$g_A(T + dT, P + dP) = g_B(T + dT, P + dP)$.

Recall a definition in calculus:

$g_A(T + dT, P + dP) - g_A(T,P) = dg_A$
$g_B(T + dT, P + dP) - g_B(T,P) = dg_B$

Thus, for the two points (T, P) and (T + dT, P + dP) on the phase boundary, the two phases have the equal value of the change in the Gibbs function:

$dg_A = dg_B$.

Recall the identities:

$dg_A = -s_A dT + v_A dP$,
$dg_B = -s_B dT + v_B dP$.

Thus,

$-s_A dT + v_A dP = -s_B dT + v_B dP$.

Rearranging, we obtain that

$dP(T)/dT = (s_B - s_A)/(v_B - v_A)$.

This result is called the *Clapeyron equation*, which relates the slope of the phase boundary to the entropy of phase change and the volume of phase change.

Liquid-solid phase boundary. The right side of the equation is approximately independent of temperature. Thus, the liquid-solid phase boundary is approximately a straight line, with the slope given by the right side of the Clapyron equation. For H_2O molecules, the specific volume is smaller in water than in ice:

$v_f - v_s = - 0.000091\ m^3/kg$.

The specific entropy is larger in liquid water than in ice:

$s_f - s_s$ = 1.22 kJ/K/kg.

Inserting these values into the Clapyron equation, we obtain the slope for the ice-water phase boundary:

dP/dT = - 13 MPa/K.

Consequently, the melting point decreases when ice is under pressure.

Exercise. YouTube Why is ice slippery? At 1:41 of the video, the host attempts to explain why ice is slippery. This explanation is held among many people. But is it right? Will the weight of a skater be enough to lower melting temperature enough to melt ice?

Exercise. YouTube regelation, regelation (another take). How does regelation work? Wiki regelation.

Exercise. Apply the Clapyron equation to the liquid-gas and solid-gas phase boundaries.

Breed thermodynamic relations like rabbits

For closed systems, we often use ten quantities: S, U, V, P, T, H, F, G, Q, W. Of the ten quantities, the first eight are functions of state (i.e., properties), but Q and W are not. The states of a closed system are specified by two independent properties. There are billions and billions of thermodynamic relations among the ten quantities and their derivatives. Most of these relations have not found any use, but a small collections have. A few useful relations are described above.

P.W. Bridgman, A complete collection of thermodynamic formulas. Physical Review 3, 273, 1914.

Van der Waals model of liquid-gas phase transition

The ideal gas model represents real gases well at high temperature and low pressure, when individual molecules are far apart on average. However, at low temperature and high pressure, when the molecules nearly condense, the ideal gas model does not describe real gases well.

Equation of state, P(T,V)

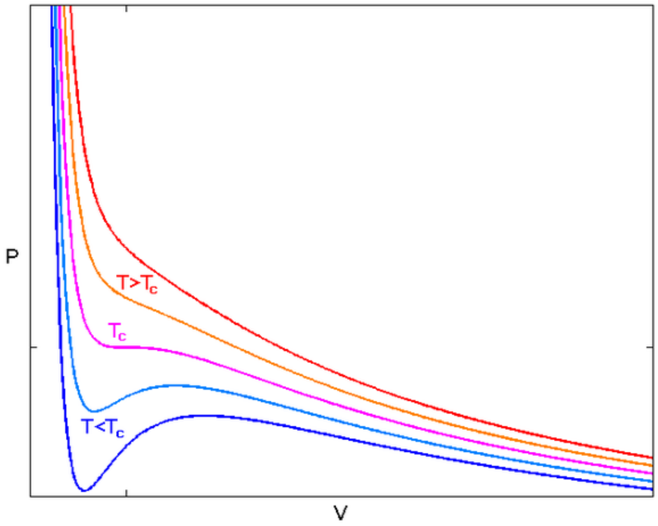
van der Waals (1873) modified the ideal gas law as follows:

$P = kT/(V - b) - a/V^2$.

Here V is the volume of the container divided by the number of molecules.

As we will see, a represents the attraction between molecules, and b represents the finite volume of each individual molecule. The model explains the origin of the liquid-gas phase change.

When a = 0 and b = 0, the van der Waals equation of state reduces to the ideal gas law, PV = kT.



(Figure taken from the Wikipedia page on van der Waals equation, plotted for some values of a and b.)

Critical state

For a constant temperature T, the van der Waals equation corresponds to a curve on the pressure-volume plane. An isotherm at a high temperature is a monotonic curve. An isotherm at a low temperature has a minimum and a maximum. When the minimum and the maximum collide, the fluid reaches the critical state.

Recall a fact in calculus. At the minimum and the maximum of an isotherm, the following condition holds:

$\partial P(T,V)/\partial V = 0$.

Recall another fact in calculus. Near the minimum, the isotherm is convex down, $\partial^2 P(T,V)/\partial V^2 > 0$. Near the maximum, the isotherm is convex up, $\partial^2 P(T,V)/\partial V^2 < 0$. The minimum and maximum collide when

$\partial^2 P(T,V)/\partial V^2 = 0$.

Thus, the critical state satisfy three equations:

$P = kT/(V - b) - a/V^2$,
$- kT/(V - b)^2 + 2a/V^3 = 0$,
$2kT/(V - b)^3 - 6a/V^4 = 0$.

Solving these three equations, we obtain that

$V_c = 3b$, $kT_c = 8a/(27b)$, $P_c = a/(27b^2)$.

These equations express the critical volume, temperature, and pressure in terms of the constants a and b.

Helmholtz function

The van der Waals model prescribes the function $P(T,V)$. Recall that T and V are also the independent variables of the Helmholtz function, $F(T,V)$. Integrate the identity $-P = \partial F(T,V)/\partial V$, and we obtain that

$F(T,V) = - kT \log(V - b) - a/V + Z(T)$.

The integration is over V, but F is a function of T and V. Consequently, the constant of this integration is a function of temperature, $Z(T)$.

Using the Helmholtz function $F(T,V)$, we can determine all other thermodynamic properties as functions of T and V.

Entropy

Recall the identity $-S = \partial F(T,V)/\partial T$. We obtain that

$S(T,V) = k \log(V - b) - dZ(T)/dT$.

At a fixed temperature, the number of quantum states per molecule is proportional to $(V - b)$. Thus, b represents the size of an individual molecule.

Energy

Recall the definition of the Helmholtz function, $F = U - TS$. We obtain that

$U(T,V) = - a/V + Z(T) - TdZ(T)/dT$.

Note that V is the volume of the container divided by the number of molecules. Thus, 1/V is the number density of molecules in the container. The van der Waals model assumes that the intermolecular attraction reduces the internal energy by an amount proportional to the number density of the molecules. This seems to be a reasonable first-order approximation. Whereas the internal energy of an ideal gas is independent of volume, the internal energy of a van der Waals gas depends on both volume and temperature.

Thermal capacity. Recall the definition of thermal capacity, $C_V = \partial U(T,V)/\partial T$. In general, the thermal capacity of a pure substance is a function of temperature and volume, $C_V(T,V)$. Inserting the expression for thermal energy, we obtain that

$C_V = - Td^2Z(T)/dT^2$.

In the van der Waals model, the thermal capacity C_V is a function of temperature only, independent of volume.

Competition between entropy and energy

We next fix temperature, and focus on F(T,V) as a function of V. Entropy and energy compete to bend the curve F(T,V). The term $- kT \log(V - b)$ comes from the entropy of the molecules, and is convex downward, which stabilizes a homogeneous state. The term $-a/V$ comes from the intermolecular attraction, and is convex upward, which destabilizes a homogeneous state.

Entropy tends to disperse molecules and favors gas. Energy (i.e., intermolecular attraction) tends to aggregate molecules and favors liquid.

At a high temperature, the entropy prevails for all values of volume, so that the entire curve F(T,V) is convex downward, and the entire curve P(T,V) is monotonic.

At a low temperature, the entropy prevails for small and large values of volume, so that only these parts of the curve F(T,V) is convex downward, and only these parts of the curve P(T,V) is monotonic.

The thermodynamics of a pure substance is fully characterized by the Helmholtz function, F(T,V). In the above, we have started from the van der Waals equation, and examined its consequences for energy and entropy. Since the physical interpretation of the two terms aN^2/V

and Nb are quite reasonable, we may as well use them as a starting point to derive the van der Waals equation.

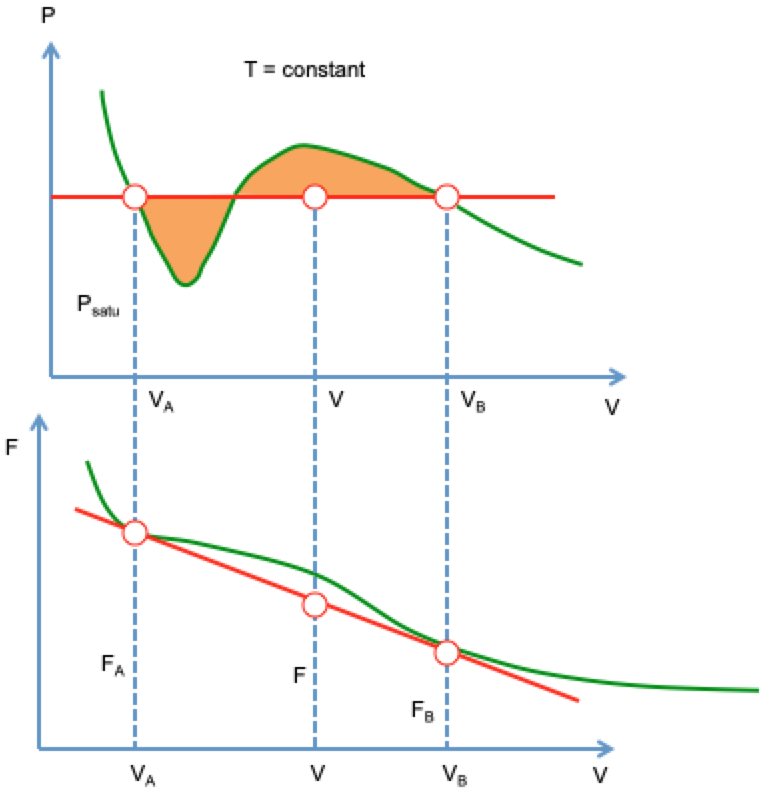
Maxwell rule

A convex-upward part of the F(T,V) curve corresponds to a phase transition. Draw a line tangent to the F(T,V) curve at two points A and B. The two tangent points correspond to two homogeneous states in equilibrium at the same pressure, P_{satu}. This pressure corresponds to the slope of the tangent line:

$F_A - F_B = P_{satu}(V_B - V_A)$.

This equation can be interpreted on the pressure-volume plane: $F_A - F_B$ is the area under the curve P(T,V) between states A and B, and $P_{satu}(V_B - V_A)$ is the area of a rectangle. The equality of the two areas requires that P_{satu} be placed at the level that equate the two shaded areas. This construction is called the *Maxwell rule*.

Both F and V are extensive properties. The F-V plane is a two-dimensional vector space. A mixture of homogeneous states obeys the rules of mixture. Of the total of N molecules, N_A molecules are in homogeneous state A, and N_B molecules are in homogeneous state B. The mixture of the two homogeneous states correspond to a point on the tangent line, located at the center of gravity according to N_A and N_B.



Exercise. In the van der Waals model, assume a constant thermal capacity C_V. Find the function S(U,V). Plot this function around the critical state using some values of a, b, and C_V.

Exercise. A generalized van der Waals model takes the form P = Tw(V) + q(V), where w(V) and q(V) are two functions of V to fit the experimental data. Calculate the functions F(T,V), S(T,V), and U(T,V). Interpret the significance of the two functions w(V) and q(V) in terms of entropy and energy.

Exercise. The van der Waals model does not fit experimental data accurately. Clausius proposed a different model: $P = kT/(V - b) - a/[T(V + c)^2]$. Here V is the volume of the container divided by the number of molecules. Calculate the functions F(T,V), S(T,V), and U(T,V). Interpret a, b, c in terms of energy and entropy. Express the critical temperature, pressure, and volume in terms of a, b, c.

Nobel Lecture. Van der Waals, The equation of state for gases and liquids, 1910.

From ideal gas to real fluid, multicomponent materials, and materials genome

Ideal gas. The thermodynamics of an ideal gas is fully specified by two equations:

$PV = Nk_BT$
$dU = Nc_V(T)dT.$

But the ideal gas law describes a substance only at high temperatures and low pressures.

Van der Waals model. The Helmholtz function F(T,V) lets us calculate all other thermodynamic properties as functions of T and V. For example, the relation $P = - \partial F(T,V)/\partial V$ calculates the function P(T,V).

The van der Waals model can be expressed as a Helmholtz function:

$F(T,V) = - kT \log(V - b) - a/V + Z(T).$

The function contains two constants a and b, and a function Z(T). The constants a and b and the function Z(T) are left to fit with experimental data. For example, a and b can be used to fit the measured P(T,V) function, and Z(T) can be used to fit the measure thermal capacity.

Steam tables then and now. The International Association for the Properties of Water and Steam (IAPWS) is an international association of national organizations concerned with the properties of water and steam. The following short documents describe the history and contemporary practice of constructing steam tables.

- Allen H. Harvey, Steam Tables
- Revised release on the IAPWS formulation 1995

Big data. Of course, the van der Waals model is still too simplistic to fit data accurately. The IAPWS prescribes a form of the Helmholtz function F(T,V) with eighty-some coefficients, which are fit to experimental data. Constructing the steam tables dates back more than 200 years, and is perhaps the first big-data project. Thermodynamics teaches us how to obtain, curate, and use properties.

The Helmholtz function of a similar form has been adopted to fit data of numerous other pure substances (NIST software).

The approach has been extended to multi-component substances, and is called the CALPHAD method. Here, a form of the Gibbs function is assumed as a function of T, P, and composition. The function contains coefficients to fit experimental data.

In 2011, President Obama announced the Material Genome Initiative.

Exercise. A well-insulated, rigid tank is divided into two rooms by a rigid membrane. Room A has a volume of 1 m^3, and contains a water-seam mixture at a temperature of 200 C and a quality of 50%. Room B has a volume of 2 m^3, and contains a water-steam mixture at a temperature of 300 C and a quality of 90%. The membrane now ruptures and the H_2O molecules come to a final state of equilibrium. Determine the volume, energy, entropy, pressure, temperature, and quality of the final state. Compare the entropies of the initial and final state. You may wish to use a property calculator.

Slides: carnot cycle

Slides: control volume

BAT on various processes

We now run the basic algorithm of thermodynamics (BAT) on various processes. At the end of the analysis of each process, we define a *second-law efficiency*, which ranks the efficiency of the process in converting expense to product.

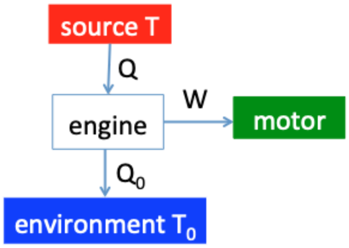
This application of the basic algorithm of thermodynamics has gained popularity in recent decades. The idea dates back to Gibbs (1873) and Carnot (1824).

This method of analysis has numerous names, including *second-law analysis*, *availability analysis*, *exergy analysis*, and *entropy-generation analysis*.

Engine

In study a general method of analysis, it is good to commit a few concrete examples to memory. Let us analyze an engine again, and place ideas in perspective.

We run the basic algorithm of thermodynamics in four steps.



Step 1. Identify an isolated system with independent internal variables. Here we identify an isolated system that has four parts:

1. Engine, modeled as a closed system running in cycles, capable of transferring energy by heat and by work
2. Source, modeled as a thermal reservoir of a fixed high temperature T
3. Environment, modeled as a thermal reservoir of a fixed low temperature T_0
4. Motor, modeled as a device capable of transferring energy by work but not by heat

The isolated system has three internal variables, each playing a distinct role:

- Q. The energy transferred from the source to the engine is the *expense*.
- Q_0. The energy transferred from the engine to the environment is the *waste*.
- W. The energy transferred from the engine to the motor is the *product*.

Not all internal variables are independent. We eliminate dependent internal variables by the principles of the conservation of energy, space, matter, and charge. In this example, only the conservation of energy gives a useful result. The isolated system conserves energy:

$0 - Q + Q_0 + W = 0$.

This equation applies to each cycle. Each term is the change in energy of one part of the isolated system. The engine runs in cycles, and returns to its initial state after each cycle, so that the engine does not change energy after each cycle. The source loses energy Q, the environment gains energy Q_0, and the motor gains energy W.

The conservation of energy relates the three internal variables, so that only two of them are independent internal variables, taken to be Q and W. Thus, $Q_0 = Q - W$. That is, we take the expense Q and product W as independent internal variables, and take the waste Q_0 as a dependent internal variable.

Step 2. Calculate the subset entropy of the isolated system as a function of the independent internal variables. The subset entropy of the isolated system is

$S_{gen} = 0 - Q/T + Q_0/T_0 + 0$.

This equation also applies to each cycle. We call the subset entropy of the isolated system the *entropy generation*, S_{gen}. Each term is the change in entropy of one part of the isolated system. The engine returns to its initial state after each cycle, so that the engine does not change entropy after each cycle. On losing energy Q, the source decreases its entropy by Q/T. On gaining energy Q_0, the environment increases its entropy by Q_0/T_0. The motor does not change entropy.

Recall $Q_0 = Q - W$. Write the entropy generation as a function of independent internal variables Q and W:

$S_{gen} = Q(1/T_0 - 1/T) - W/T_0$.

Step 3. An isolated system undergoing a reversible process does not generate subset entropy. Setting $S_{gen} = 0$ in the expression for S_{gen}, we obtain that

$W_{rev} = Q(1 - T_0/T)$.

The subscript "rev" indicates that this work is produced by a reversible process of the isolated system. The quantity W_{rev} is called the *reversible work*.

Setting $S_{gen} = 0$ also gives $Q/T = Q_0/T_0$. When the engine runs a reversible process, the isolated system generates no entropy, but merely transfers entropy from one part of the isolated system (the high-temperature thermal reservoir) to another part of the isolated system (the low-temperature thermal reservoir). This transfer of entropy degrades thermal energy, but is compensated by an upgrade—the production of work.

Step 4. An isolated system undergoing an actual process is irreversible and generates subset entropy. Setting $S_{gen} > 0$ in the expression for S_{gen}, we obtain that

$W < Q(1 - T_0/T)$.

The left side is the actual work produced by the engine. The right side is the reversible work.

Irreversible processes. An isolated system generates subset entropy by irreversible processes like friction, energy transfer between bodies of finite difference in temperature, and energy transfer between bodies of finite difference in pressure.

The basic algorithm of thermodynamics does not specify any irreversible process. In the analysis, all irreversible processes are lumped in a single number, the entropy generation S_{gen}. The equation $S_{gen} = Q(1/T_0 - 1/T) - W/T_0$ says that the irreversible processes cause the actual work to be smaller than the reversible work. Thus, given Q, the reversible work is the maximum work.

Means to realize the reversible work. The basic algorithm of thermodynamics does not specify any mechanism to realize the reversible work. In the analysis, the engine is represented by a box, with arrows in and out.

The reversible work can be approximately realized by physical mechanisms. For example, Carnot described a reversible engine using a fluid in a piston-cylinder setup. The setup undergoes reversible cycles. Each cycle consists of an isothermal process at T, an adiabatic process from T to T_0, an isothermal process at T_0, and an adiabatic process from T_0 to T. To be reversible, the Carnot cycle avoids all irreversible processes. In particular, the Carnot cycle avoids any thermal contact between bodies of different temperatures. See slides on Carnot cycle.

First-law efficiency. Define the *thermal efficiency* by the ratio of two terms of energy:

$\eta_{\text{1st law}}$ = (output energy)/(input energy).

Thermal efficiency is also called *energy efficiency*, or *first-law efficiency*.

The thermal efficiency for an engine is W/Q. Write the inequality $W < Q(1 - T_0/T)$ as

$W/Q < 1 - T_0/T$.

The left side is the thermal efficiency of an actual engine, and the right side is the Carnot efficiency of a reversible engine. The Carnot efficiency limits the thermal efficiency.

Second-law efficiency. Look again at entropy generation:

$S_{gen} = Q(1/T_0 - 1/T) - W/T_0$.

An engine expends heat Q and produces work W. The above equation splits entropy generation into two parts, one part for the expense, and the other part for the product. The expense increases S_{gen}, and the product decreases S_{gen}.

Define the *second-law efficiency* by the ratio of the two parts of entropy generation:

$\eta_{\text{2nd law}}$ = (product)/(expense).

The second-law efficiency for the engine is

$\eta_{\text{2nd law}} = (W/T_0)/(Q(1/T_0 - 1/T)) = W/W_{rev}$.

The second-law efficiency reaches 1 for a reversible engine, and is less than 1 for an actual engine.

General definition of the second-law efficiency. We will look at a few more devices and define a second-law efficiency for each. In each case, write

S_{gen} = (expense) - (product).

Associate part of S_{gen} to the product, and the rest of S_{gen} to the expense. Both expense and product are nonnegative.

An isolated system undergoing a reversible process does not generate entropy, $S_{gen} = 0$, and (expense) = (product).

An isolated system undergoing an irreversible process generates entropy, $S_{gen} > 0$, and (expense) > (product).

Define the second-law efficiency by

$\eta_{2nd\ law}$ = (product)/(expense).

The second-law efficiency ranks devices in terms of entropy, and is always between 0 and 1.

The first-law efficiency ranks devices in terms of energy, and can be any positive number.

Exergy and irreversibility. The reversible work is also called *available work*, *available energy*, or *exergy*. The quantity is given a distinct symbol:

$\Phi = Q(1 - T_0/T)$.

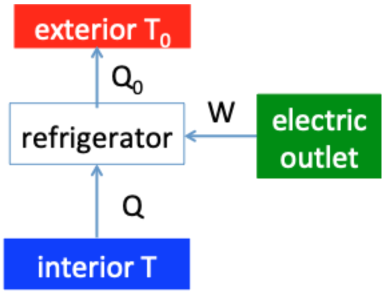
The quantity T_0S_{gen} is called *irreversibility*, and given a distinct symbol:

$I = T_0S_{gen}$.

Both exergy Φ and irreversibility I are shadows of entropy. Thermodynamics becomes needlessly complicated if people create multiple names—in words and in symbols—for every shadow of entropy. Let no shadows distract our attention from the real thing—entropy.

Refrigerator

We now analyze a refrigerator using the basic algorithm of thermodynamics.



*Step 1***.** We identify an isolated system that has four parts:

1. Refrigerator, modeled as a closed system running in cycles, capable of transferring energy by work and by heat
2. Interior, modeled as a thermal reservoir of a low temperature T
3. Exterior, modeled as a thermal reservoir of a high temperature T_0
4. Electric outlet, modeled as a mechanism capable of supplying energy without changing entropy

The isolated system has three internal variables, which play the following roles:

- The energy Q removed from the interior is the product.
- The energy Q_0 rejected to the exterior helps to the removal from the interior.
- The energy W transferred from the outlet is the expense.

The isolated system conserves energy:

$0 - Q + Q_0 - W = 0$.

Each term is the change in energy of one part of the isolated system. Note the sign in front of W: the electric outlet transfers energy out.

Step 2. The isolated system generates subset entropy:

$S_{gen} = 0 - Q/T + Q_0/T_0 + 0$.

Each term is the change in entropy of one part of the isolated system.

Eliminating Q_0 from the above two equations, we obtain that

$S_{gen}= - Q(1/T -1/T_0) + W/T_0$.

Step 3. An isolated system undergoing a reversible process does not generate subset entropy, $S_{gen} = 0$. The expression for S_{gen} becomes that

$W_{rev} = Q(1 -T_0/T)$.

The subscript "rev" indicates that this work is produced by a reversible engine. The quantity W_{rev} is called the reversible work.

Step 4. An isolated system undergoing an actual process is irreversible and generates entropy, $S_{gen} > 0$. The expression for S_{gen} becomes that

$Q(1 -T_0/T) < W$.

The left side is the reversible work, and the right side is the actual work.

Irreversible processes and reversible refrigerator. Comments similar to those on an engine apply to a refrigerator. A Carnot cycle running in reverse is a refrigerator.

First-law efficiency. We also write the above inequality as

$Q/W < T/(T_0 - T)$.

The left side is the coefficient of performance, and the right side is the Carnot limit of the coefficient of performance. The coefficient of performance can be any nonnegative number. The ratio Q/W is the first-law efficiency of refrigerator.

Second-law efficiency. Look again at the expression for entropy generation:

$S_{gen} = - Q(1/T - 1/T_0) + W/T_0$.

A refrigerator is a work-consuming device, expending the work W from the electric outlet, and producing the removal of the heat Q from the interior. Recall the definition of the second-law efficiency:

$\eta_{\text{2nd law}}$ = (product)/(expense).

Thus, the second-law efficiency of the refrigerator is

$\eta_{\text{2nd law}} = (Q(1/T - 1/T_0))/(W/T_0) = W_{rev}/W$.

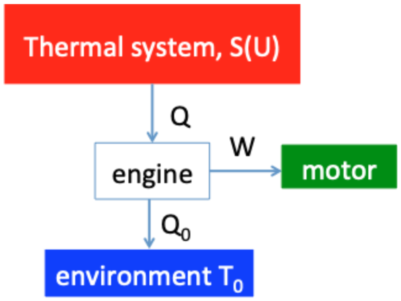
The second-law efficiency is between 0 and 1.

Exercise. A refrigerator maintains an interior temperature of -10 Celsius, and the temperature in the environment is 20 Celsius. The thermal energy leaks into the refrigerator at the rate of 100 W. The compressor consumes electric energy at the rate of 20 W. Determine the actual coefficient of performance, the Carnot limit of the coefficient of performance, and the second-law efficiency.

Exercise. A heat pump runs in cycles to transfer energy from a cold environment to a warm interior. Use the basic algorithm of thermodynamics to derive the expression for the second-law efficiency of a heat pump. Compare the second-law efficiency to the coefficient of performance and the Carnot limit of coefficient of performance.

Thermal system

We now analyze a thermal system using the basic algorithm of thermodynamics.



Step 1. We construct an isolated system that has four parts:

1. Thermal system, characterized by a function S(U).
2. Environment, modeled modeled as a thermal reservoir of temperature T_0
3. Engine, a mechanism running in cycle, capable of transferring energy by heat and by work
4. Device, modeled as a mechanism capable of receiving energy without changing entropy

The isolated system has several internal variables:

- energy $Q = U - U_0$ lost by the thermal system,
- energy W received by the motor, and
- energy Q_0 received by the environment.

The thermal system is initially in a state of particular values of S, U, and T. An environment has a fixed temperature T_0. So long as the thermal system and the environment have different temperatures, $T \neq T_0$, we can run an engine between the two temperatures and extract work. Once the thermal system equilibrates with the environment, no thermodynamic change is possible, and the thermal system is said to be in the *dead state*. Let S_0, U_0, and T_0 be the properties of the thermal system at the dead state. What is the maximum work that can be produced as the thermal system changes from the initial state to the dead state?

The isolated system conserves energy:

$$(U_0 - U) + Q_0 + 0 + W = 0.$$

Each term is the change in energy of one part of the isolated system from the initial state to the dead state. The engine runs in cycles and does not change state after each cycle.

Step 2. The isolated system generates subset entropy:

$$S_{gen} = (S_0 - S) + Q_0/T_0 + 0 + 0.$$

Each term is the change in entropy of one part of the isolated system from the initial state to the dead state. The engine runs in cycles and does not change state after each cycle. The motor does not change entropy. All irreversible processes of the isolated system contribute to S_{gen}.

Eliminating Q_0 from the above two equations, we obtain that

$S_{gen} = (U - U_0)/T_0 - (S - S_0) - W/T_0$.

Step 3. The isolated system undergoing a reversible process does not generate entropy, $S_{gen} = 0$, and achieves the reversible work:

$W_{rev} = (U - U_0) - T_0(S - S_0)$.

Step 4. The isolated system undergoing an actual process is reversible and generates entropy, $S_{gen} > 0$, so that the actual work is below the reversible work:

$W < (U - U_0) - T_0(S - S_0)$.

Mechanisms to realize reversible work. A cup of coffee is a thermal system. Initially it is hotter than the environment. The coffee cooling in the environment produces no work. But the difference in temperature between the coffee and the environment let us run an engine. In class, I run this Stirling engine on a cup of hot coffee.

The cup of coffee lowers the temperature as the coffee gives off energy to the engine. Consequently, the engine cannot run in cycles. To approach the reversible work, we run the engine slowly, so that the engine undergoes approximate cycles. Each approximate cycle takes infinitesimal amount of energy from the coffee, and infinitesimally lowers the temperature of the coffee. Over infinitely many such cycles, the temperature of the coffee approaches that of the environment, and the total output work approaches the reversible work. Of course, we must avoid all other irreversible processes.

Second-law efficiency. Recall the definition of the second-law efficiency:

$\eta_{2nd\ law}$ = (product)/(expense).

Look again at the equation $S_{gen} = (U - U_0)/T_0 - (S - S_0) - W/T_0$. Associate the last part to the product, and the rest to the expense. Thus, the second-law efficiency of the thermal system is

$\eta_{2nd\ law} = W/W_{rev}$.

Exergy. Call the reversible work of the thermal system the exergy. Write

$\Phi = (U - U_0) - T_0(S - S_0)$.

The exergy of a thermal system is reminiscent of the Helmholtz function. The difference is as follows. The exergy involves two states of a thermal system at different temperatures. The Helmholtz function involves a thermal system at a fixed temperature. Both exergy and Helmholtz functions are shadows of entropy. Let no shadow distract us from the real thing—entropy.

Exercise. 1 kg of water is initially at 90 Celsius and cools by transferring energy to the environment at 25 Celsius. Determine the reversible work for this process. Assume a constant specific thermal capacity of 4.18 kJ/kg-K for water.

Exercise. I can also reword the above exercise as follows. Estimate the reversible work of a cup of coffee.

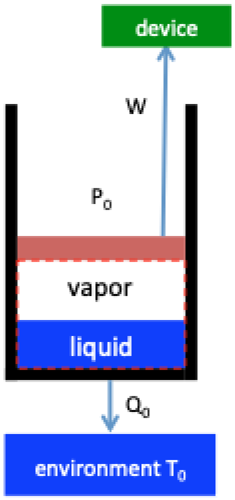
Exercise. Engine can run on ice. YouTube Stirling engine. 1 kg of ice is initially at - 20 Celsius and warms by receiving energy from the environment at 25 Celsius. Determine the reversible work for this process. Assume a constant specific thermal capacity of 4.18 kJ/kg-K for water, a constant specific thermal capacity of 2.06 kJ/kg-K for ice, and an energy of melting of 334 kJ/kg.

Exercise. Interprete $W_{rev} = (U - U_0) - T_0(S - S_0)$ on the energy-entropy plane. Consider two cases, $T > T_0$ and $T < T_0$.

Exercise. What is the first-law efficiency of a thermal system?

Closed system

We now analyze a closed system using the basic algorithm of thermodynamics.



Step 1. We construct an isolated system of four parts:

1. Closed system, characterized by a function S(U,V).
2. Mechanical environment, modeled as a weight that gives a fixed pressure P_0
3. Thermal environment, modeled as a thermal reservoir of temperature T_0
4. Device, modeled as a mechanism capable of receiving energy without changing entropy

The closed system is in a thermodynamic state of particular values of S, U, V, P, T, ect. An environment has a fixed temperature T_0 and a fixed pressure P_0. Once the closed system equilibrates with the environment, no thermodynamic change is possible. The closed system is said to be in the *dead state*. What is the maximum work that can be produced as the closed system approaches the dead state?

The isolated system has several Internal variables: energy U and volume V of the closed system, potential energy of the weight, W, thermal energy received by the environment, Q_0.

The isolated system conserves energy:

$(U_0 - U) + P_0(V_0 - V) + Q_0 + W = 0$

Each term is the change in energy of a part of the isolated system from the initial state to the dead state.

Step 2. The isolated system generates subset entropy:

$S_{gen} = (S_0 - S) + 0 + Q_0/T_0 + 0.$

Each term is the change in entropy of a part of the isolated system from the initial state to the dead state.

Eliminating Q_0 from the above two equations, we obtain that

$S_{gen} = (U - U_0)/T_0 +(V - V_0)P_0/T_0 - (S - S_0) - W/T_0$

Step 3. A reversible process is isentropic, $S_{gen} = 0$, and achieves the reversible work:

$W_{rev} = (U - U_0) + P_0(V - V_0) - T_0(S - S_0).$

Step 4. An actual process generates entropy, $S_{gen} > 0$, so that the actual work is below the reversible work:

$W < (U - U_0) + P_0(V - V_0) - T_0(S - S_0).$

Second-law efficiency. Recall the definition of the second-law efficiency:

$\eta_{2nd\ law} = (product)/(expense).$

The second-law efficiency of the closed system is

$\eta_{2nd\ law} = W/W_{rev}.$

Exergy. Call the reversible work of the closed system the exergy. Write

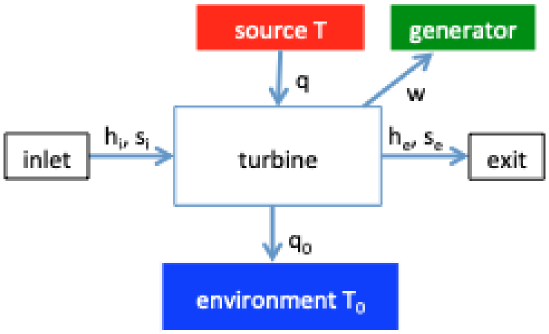
$\Phi = (U - U_0) + P_0(V - V_0) - T_0(S - S_0).$

The exergy of a closed system is reminiscent of the Gibbs function. They are both shadows of entropy. The difference is as follows. The exergy involves two states of a closed system at different temperatures and different presumes. The Gibbs function involves a closed system at a fixed temperature and a fixed pressure. Both energy and the Gibbs function are shadows of entropy.

Exercise. What is the first law efficiency of a closed system?

Turbine

A power plant contains many parts. Each part can be analyzed using the basic algorithm of thermodynamics. Let us begin with a turbine.



Step 1. We construct an isolated system that has six parts:

1. Turbine, modeled as a control volume in steady state
2. Inlet, modeled as a flow
3. Exit, modeled as a flow
4. Source, modeled as a thermal reservoir of temperature T
5. Environment, modeled as a thermal reservoir of temperature T_0
6. Generator, modeled as a mechanism to consume work without changing entropy

The isolated system has several internal variables, as labeled with arrows.

The isolated system conserves energy:

$$0 - h_i + h_e - q + q_0 + w = 0.$$

Each term is the change in energy of one part of the isolated system. The turbine in steady state does not change energy.

To account for kinetic and potential energy of the inlet and exit flows, we can replace each enthalpy with the total enthalpy:

$$h_{tot} = h + V^2/2 + Zg.$$

Step 2. The isolated system generates subset entropy:

$$s_{gen} = 0 - s_i + s_e - q/T + q_0/T_0 + 0.$$

Each term is the change in entropy of one part of the isolated system. The turbine in steady state does not change entropy. The generator does not change entropy.

Eliminating q_0 from the above two equations, we obtain that

$s_{gen} = (h_i/T_0 - s_i) - (h_e/T_0 - s_e) + q(1/T_0 - 1/T) - w/T_0$.

Step 3. A reversible process of the isolated system does not generate subset entropy, $s_{gen} = 0$, so that the actual work reaches the reversible work:

$w_{rev} = (h_i - T_0s_i) - (h_e - T_0s_e) + q(1 - T_0/T)$.

Step 4. An actual process of the isolated system generates subset entropy, $s_{gen} > 0$, so that the actual work reaches the reversible work:

$w < (h_i - T_0s_i) - (h_e - T_0s_e) + q(1 - T_0/T)$.

The left side is the actual work produced by the steady flow, and the right side is the reversible work.

Irreversible processes. In my drawing of the isolated system, the turbine can transfer energy to the environment, which is modeled as a thermal reservoir of temperature T_0. In practice, the turbine is thermally insulated, but some energy may still escape. The transfer of energy between bodies of different temperatures generates entropy. Inside turbine, friction is inevitable between moving parts. This analysis lumps all these irreversible processes into a single number, the entropy generation, s_{gen}.

Means to achieve the reversible work. To achieve the reversible work, we must remove all irreversible processes inside the turbine. Furthermore, we cannot allow the turbine to be in direct thermal contact with the environment. Because the turbine and the environment have different temperatures, we can operate a Carnot engine between them. The work out of the Carnot engine contributes to the reversible work.

Second-law efficiency. Look again at the expression for entropy generation

$s_{gen} = (h_i/T_0 - s_i) - (h_e/T_0 - s_e) + q(1/T_0 - 1/T) - w/T_0$.

On the right side, the last part accounts for the product, and the rest accounts for the expense. Recall the definition of the second-law efficiency:

$\eta_{2nd\ law} = (product)/(expense)$.

Thus, the second-law efficiency of the turbine is

$\eta_{2nd\ law} = w/w_{rev}$.

An actual turbine commonly operates without any thermal reservoir, so that $q = q_0 = 0$ and $w = h_i - h_e$. Thus,

$\eta_{2nd\ law} = w/w_{rev} = (h_i - h_e)/((h_i - T_0s_i) - (h_e - T_0s_e))$.

The second-law efficiency is between 0 and 1.

Exergy of a flow. Write

$\psi_i - \psi_e = (h_i - T_0s_i) - (h_e - T_0s_e)$.

This definition serves as shorthand. This quantity is called the change in exergy of a flow. Again, exergy is a shadow of entropy. Let us stay focussed on entropy.

First-law efficiency. Recall the isentropic efficiency of turbine:

$\eta_{1st\ law} = (h_i - h_e)/(h_i - h_{es})$.

Here h_{es} is the enthalpy of a fictitious state. The pressure of the fictitious state is the actual pressure at the exit, P_e. The entropy of the fictitious state is set to be the same as the entropy of the inlet, s_i.

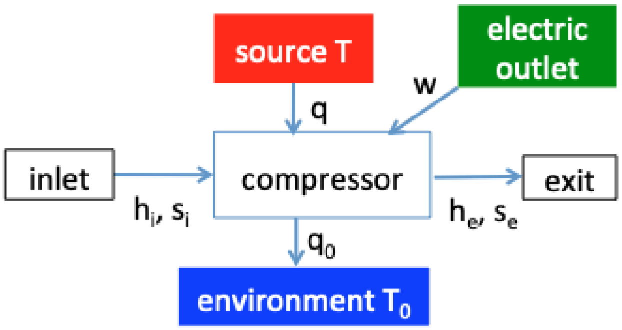
The isentropic efficiency is also called the first-law efficiency.

BS Example 8.1, 8.3, 8.5.

Exercise. For a turbine, compare the definition of isentropic efficiency and second-law efficiency.

Compressor

We now analyze a compressor using the basic algorithm of thermodynamics.



Step 1. For a work-consuming device, such as a pump or compressor, we identify an isolated system of six parts, compressor, inlet, exit, source, environment, and electric outlet.

The isolated system conserves energy:

$0 - h_i + h_e - q + q_0 - w = 0$.

Note the sign in front of w indicates that the electric outlet loses energy.

Step 2. The isolated system generates subset entropy:

$s_{gen} = 0 - s_i + s_e - q/T + q_0/T_0 + 0$.

Eliminating q_0 from the above two equations, we obtain that

$s_{gen} = (h_i/T_0 - s_i) - (h_e/T_0 - s_e) + q(1/T_0 - 1/T) + w/T_0$.

Step 3. In a reversible process, $s_{gen} = 0$, so that the actual work done by the electric outlet reaches the reversible work:

$w_{rev} = (h_e - T_0s_e) - (h_i - T_0s_i) - q(1 - T_0/T)$.

Step 4. In an actual process, $s_{gen} > 0$, so that the actual work done by the electric outlet exceeds the reversible work:

$w > w_{rev}$.

Second-law efficiency of compressor. Look again the expression for the entropy generation:

$s_{gen} = (h_i/T_0 - s_i) - (h_e/T_0 - s_e) + q(1/T_0 - 1/T) + w/T_0$.

A compressor is a work-consuming device. Recall the second-law efficiency

$\eta_{2nd\ law}$ = (product)/(expense).

Thus, the second-law efficiency of the compressor is

$\eta_{2nd\ law} = w_{rev}/w$.

A compressor commonly operates without any thermal reservoir, so that $q = q_0 = 0$ and $w = h_e - h_i$. Thus,

$\eta_{2nd\ law} = w_{rev}/w = ((h_e - T_0s_e) - (h_i - T_0s_i))/(h_e - h_i)$.

First-law efficiency. Recall the isentropic efficiency of compressor:

$\eta_{1st\ law} = (h_{es} - h_i)/(h_e - h_i)$.

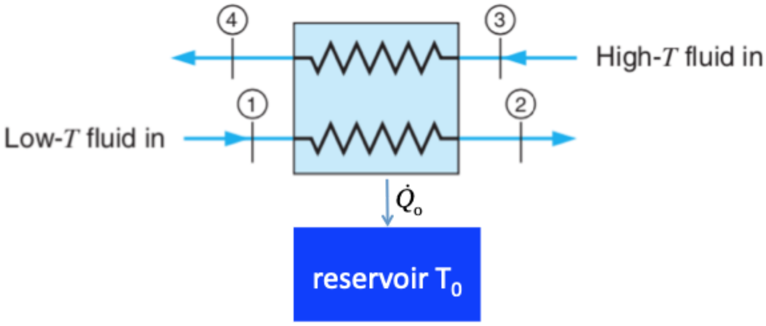
Exercise. Run the basic algorithm of thermodynamics on a nozzle and interpret the second-law efficiency $\eta_{2nd\ law} = (V_e^2/2 - V_i^2/2)/((h_i - T_0s_i) - (h_e - T_0s_e))$.

Exercise. Run the basic algorithm of thermodynamics on a diffuser and interpret the second-law efficiency $\eta_{2nd\ law} = ((h_e - T_0 s_e) - (h_i - T_0 s_i))/(V_i^2/2 - V_e^2/2)$.

Exercise. Run the basic algorithm of thermodynamics on a throttle and find the entropy generation.

Heat exchanger

In a heat exchanger, energy is transferred from a high-temperature stream to a low-temperature stream. Energy can also transfer from the heat exchanger to the environment, which is modeled as a thermal reservoir of a fixed temperature T_0.



Let us analyze this setup using the basic algorithm of thermodynamics.

Step 1. The isolated system has six parts: the control volume (i.e., the heat exchanger), the inlet and exit of the high-temperature stream, the inlet and exit of the low-temperature stream, as well as the environment of temperature T_0.

The two streams do not mix, so that each stream conserves its own mass:

$$\dot{m}_1 = \dot{m}_2$$
$$\dot{m}_3 = \dot{m}_4$$

The isolated system conserves energy:

$$\dot{m}_1(h_2 - h_1) + \dot{m}_3(h_4 - h_3) + \dot{Q}_0 = 0$$

The last term stands for the rate of energy transferred from the heat exchanger to the environment.

Step 2. The isolated system generates entropy:

$$\dot{S}_{gen} = \dot{m}_1(s_2 - s_1) + \dot{m}_3(s_4 - s_3) + \frac{\dot{Q}_0}{T_0}$$

Eliminate the heat to the environment, and we obtain that

$$\dot{S}_{gen} = \dot{m}_1\left(\left(s_2 - \frac{h_2}{T_0}\right) - \left(s_1 - \frac{h_1}{T_0}\right)\right) + \dot{m}_3\left(\left(s_4 - \frac{h_4}{T_0}\right) - \left(s_3 - \frac{h_3}{T_0}\right)\right)$$

Step 3. A reversible process of the isolated system does not generate subset entropy, so that

$$\dot{m}_1\left(\left(s_2 - \frac{h_2}{T_0}\right) - \left(s_1 - \frac{h_1}{T_0}\right)\right) + \dot{m}_3\left(\left(s_4 - \frac{h_4}{T_0}\right) - \left(s_3 - \frac{h_3}{T_0}\right)\right) = 0$$

Step 4. An actual process of the isolated system generates subset entropy, so that

$$\dot{m}_1\left(\left(s_2 - \frac{h_2}{T_0}\right) - \left(s_1 - \frac{h_1}{T_0}\right)\right) + \dot{m}_3\left(\left(s_4 - \frac{h_4}{T_0}\right) - \left(s_3 - \frac{h_3}{T_0}\right)\right) > 0$$

Second-law efficiency. Recall the definition of the second-law efficiency:

$\eta_{\text{2nd law}}$ = (product)/(expense).

What are the “expense” and “product” of a heat exchanger? Let us consider the following scenario. The heat exchanger uses the high-temperature stream to heat the low-temperature stream. Look again at the expression for the entropy generation:

$$\dot{S}_{gen} = \dot{m}_1\left(\left(s_2 - \frac{h_2}{T_0}\right) - \left(s_1 - \frac{h_1}{T_0}\right)\right) + \dot{m}_3\left(\left(s_4 - \frac{h_4}{T_0}\right) - \left(s_3 - \frac{h_3}{T_0}\right)\right)$$

The term for the high-temperature stream 34 is for the expense and is positive. The term for the low-temperature stream 12 is for the product and is negative. Thus, the second-law efficiency of the heat exchanger is

$$\eta_{\text{2nd law}} = \frac{\dot{m}_1\left(\left(s_1 - \frac{h_1}{T_0}\right) - \left(s_2 - \frac{h_2}{T_0}\right)\right)}{\dot{m}_3\left(\left(s_4 - \frac{h_4}{T_0}\right) - \left(s_3 - \frac{h_3}{T_0}\right)\right)}$$

The second-law efficiency is always between 0 and 1.

The combination $s - h/T_0$ is reminiscent of the Planck function $s - h/T$. The quantity $s - h/T_0$ involves two states: s and h are for a state in the flow, and T_0 is for the environment. By contrast, the Planck function $s - h/T$ involves a single state.

BS Example 8.6

Exercise. Run the basic algorithm of thermodynamics on a boiler and define the second-law efficiency. Assume that boiler is in contact with a thermal reservoir of a fixed temperature T_H. The environment is a thermal reservoir of a fixed temperature T_0.

Exercise. Run the basic algorithm of thermodynamics on a condenser and define the second-law efficiency.

Slides: engine and refrigerator

Ideal gas mixture

- In the beginning of the course, we have looked at moist air—an ideal gas mixture of molecules of several species.
- Let us list the equations for ideal gas mixtures here.

- Model an ideal gas mixture as a closed system.
- Specify a state of the mixture by two properties, T and V.
- We need four equations of state to express the properties P, U, S, H as functions of T and V.

- The mixture has a multiple species of molecules. Let us list equations for a mixture of two species, A and B.
- Let n_A be the number of moles of species A, and n_B be the number of moles of species B.
- $PV = (n_A + n_B)RT$. That is, the ideal gas law applies to the total number of molecules.
- $P_A = n_ART/V$ is called the partial pressure of species A.
- $P_B = n_BRT/V$ is called the partial pressure of species B.
- $U(T) = n_Au_A(T) + n_Bu_B(T)$.
- $H(T) = n_Ah_A(T) + n_Bh_B(T)$.
- $S(T,P) = n_A(s_A(T,P_0) - R\log(P_A/P_0)) + n_B(s_B(T,P_0) - R \log(P_B/P_0))$.

Psychrometrics

Do not confuse two words: psychrometrics and psychometrics. Psychrometrics is the study of moist air. Psychometrics means methods of measuring mental ability, such as an IQ test, or SAT test. Wiki psychrometrics. Wiki psychometrics.

Whereas psychrometrics has long yielded to thermodynamic analysis, psychometrics has not. I am hopeful that psychometrics will finally yield to thermodynamic analysis in coming decades, in the age of ubiquitous sensing and cloud computing. Watch out for advances, opportunities, and ethical quandaries.

This section is devoted to psychrometrics—the study of moist air. Water and air are among the most essential substances for life. Applications of psychrometrics are wide ranging, including meteorology, weather forecast, air conditioning, drying of food, drying of clothes, and cooling towers of power plants and buildings. A few simple thermodynamic considerations go a long way to enable all these applications.

Water and steam. One mole of H_2O molecules has a mass of 18 grams. The specific gas constant for water is

R_v = (8.314 kJ/kmol-K)/(18 kg/kmol) = 0.462 kJ/kg-K.

Dry air. One mole of dry air has approximately 0.79 moles of N_2 and 0.21 moles of O_2. One mole of N_2 molecules has a mass of 28 grams, and one mole of O_2 molecules has a mass of 32 grams. The specific gas constant for dry air is

R_a = (8.314 kJ/kmol-K)/(0.79 x 28 kg/kmol + 0.21 x 32 kg/kmol) = 0.288 kJ/kg-K.

Moist air. A moist air is a mixture of H_2O vapor and dry air. The composition of a moist air is specified by the mole fraction of every species of molecules in the moist air. The amount of H_2O molecules in the moist air can change greatly due to condensation of vapor to water, or evaporation from water to vapor. The relative proportions of other species of molecules, however, are assumed to be constant. In particular, we will neglect a small amount of N_2, O_2, etc. dissolved in water.

Psychrometric state

A thermodynamic state of moist air is specified by *three* independent thermodynamic properties. For the time being, we choose the following three properties: pressure, temperature, and composition. The pressure P of a moist air is also called *barometric* pressure. For a reason to be explained shortly, the temperature T of a moist air is called the *dry bulb temperature*. The composition of a moist air is specified by

(mass of H_2O molecules)/(mass of all other species of molecules)

This ratio is called the *humidity ratio*, denoted by

$\omega = m_v/m_a$.

Here m_v is the mass of H_2O vapor in the moist air, and m_a is the mass of all other species of molecules in the moist air. The humidity ratio is also called the absolute humidity, specific humidity, and water content.

These alternative names are needless complications. We may as well call the three properties pressure P, temperature T, and humidity ω. A value of the triple, (P,T,ω), specifies a state of moist air.

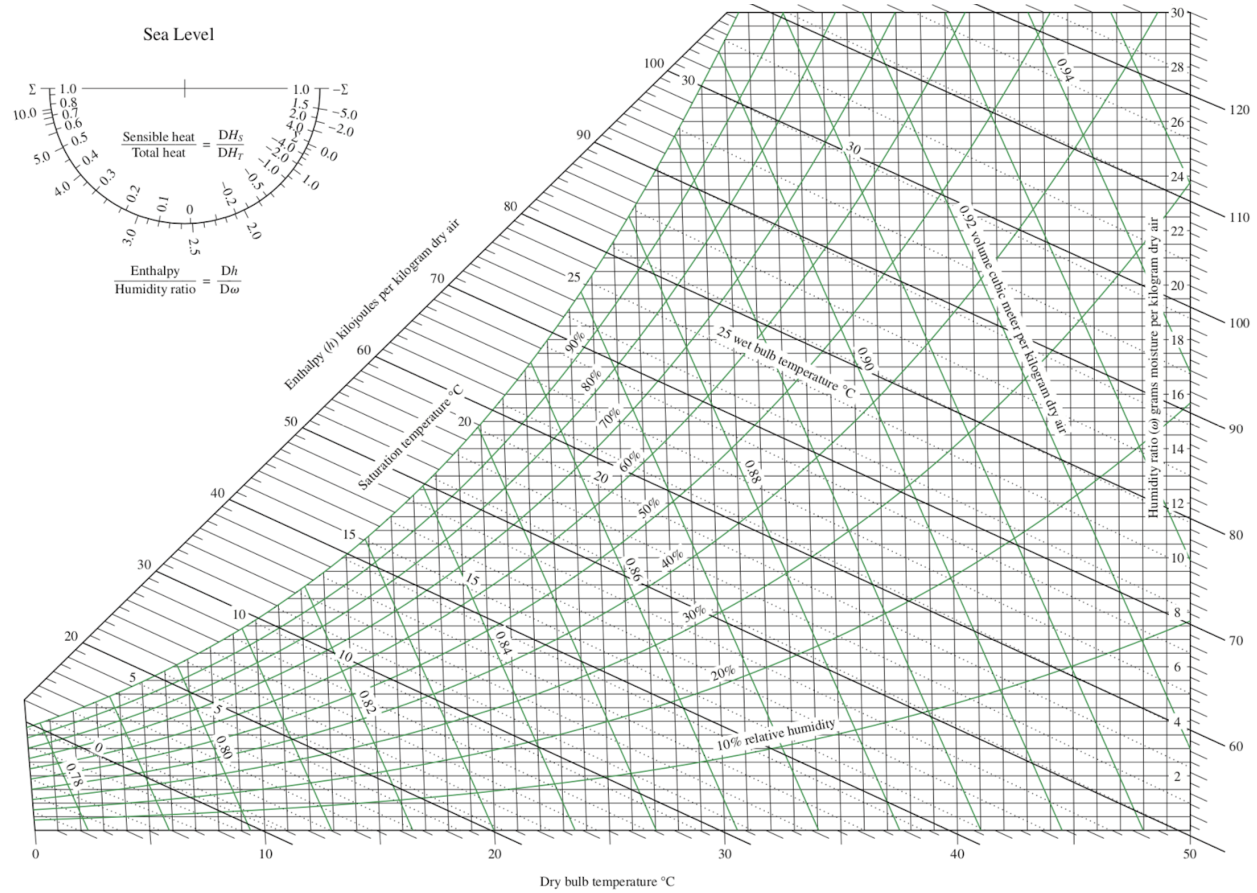
Psychrometric chart

Three properties are one property too many to represent the states of moist air on a plane. We compromise.

The pressure of air P is caused by the weight of air. Consequently, the pressure of air changes with elevation. At the elevation of sea level, the pressure is approximately P = 100 kPa. We will focus on applications at the pressure of P = 100 kPa. At this pressure, a state of moist air is specified by two properties: the temperature T, and the humidity ω.

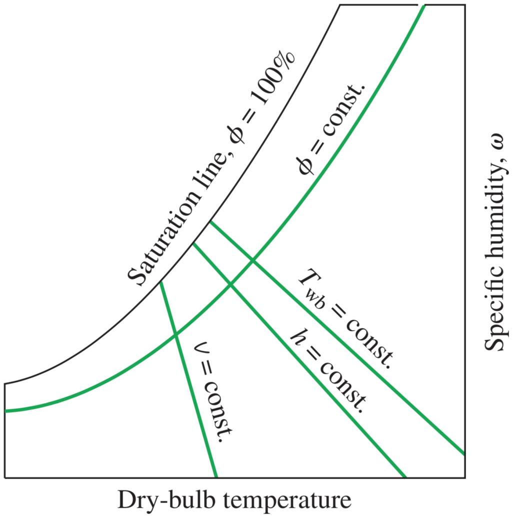
A psychrometric chart (Carrier, 1904) uses the temperature T as the horizontal axis, and uses the humidity ω as the vertical axis. Each point on the T-ω plane corresponds to a state of moist air. We need one T-ω plane for each value of pressure P.

- YouTube How to draw a psychrometric chart.
- A set of psychrometric charts.
- A large number of psychrometric apps exist, some are free.



Psychrometric property

A state of moist air has many thermodynamic properties. Each property is a function of the three independent properties: the pressure P, temperature T, and humidity ω. Let us look at several commonly used properties, and express each property as a function of P, T, and ω.



Specific volume of moist air, v. Model a moist air as an ideal gas. The ideal gas law for the mixture is

$PV = (m_v R_v + m_a R_a)T$.

Define the specific volume of the moist air by

(specific volume of moist air) = (volume of moist air)/(mass of the dry air).

Denote the specific volume of the moist air by

$v = V/m_a$.

Thus

$v = (\omega R_v + R_a)T/P$.

Thus, v is a function of P, T, and ω. On the T-ω plane of P = 100 kPa, the lines of constant v are nearly straight lines, in the small range of temperature in practical applications.

Partial pressure of water vapor in the moist air, P_v. In the moist air, let the partial pressure of the water vapor be P_v, and the partial pressure of air be P_a. Their sum is the (barometric) pressure:

$P_v + P_a = P$.

Recall the ideal gas law:

$P_vV = m_vR_vT$,
$P_aV = m_aR_aT$.

The ratio of the two equations gives that

$\omega = m_v/m_a = (R_a/R_v)(P_v/P_a) = 0.622P_v/P_a$.

Write

$\omega = 0.622P_v/(P- P_v)$.

Thus, P_v is a function of P and ω. On the T-ω plane of P = 100 kPa, the lines of constant P_v are horizontal lines.

Relative humidity, **ϕ**. Define the relative humidity by

(relative humidity) = (partial pressure of water vapor)/(saturated pressure of water).

Denote the relative humidity by

$\phi = P_v/P_g(T)$.

Recall that the saturated pressure of water is a function of temperature, $P_g(T)$, which is listed in the steam tables. The above equation confirms that the relative humidity is a function of P, T and ω.

On the T-ω plane of P = 100 kPa, the lines of constant relative humidity are set of curves. The line of ϕ = 0 coincides with the T axis, and the line of ϕ = 100% define the upper bound of the psychrometric chart. Write

$\omega = 0.622\phi P_g(T)/(P- \phi P_g(T))$.

On the T-ω plane of P = 100 kPa, this equation defines the lines of constant ϕ, once we input the values of the function $P_g(T)$ from a steam table.

Specific enthalpy of moist air, h. The enthalpy of moist air is a sum:

$H = m_ah_a + m_vh_v$.

Define the specific enthalpy of moist air by (specific enthalpy of moist air) = (enthalpy of moist air)/(mass of the dry air).

Denote the specific enthalpy of moist air by

$h = H/m_a = h_a + \omega h_v$.

Enthalpy is a relative property. Follow a convention, we set the enthalpy of state of water in the water-ice-steam three phase equilibrium to be zero. We set the enthalpy of air to be zero at zero Celsius.

Because the range of temperature is small in psychrometrics, we adopt the following approximations:

- Water is modeled as a thermal system of constant specific thermal capacity, $c_f = 4.18$ kJ/kg-K, so that $h_f = 4.18\ T$.
- Steam (i.e., water vapor) is modeled as an ideal gas of constant thermal capacity, $c_g = 1.82$ kJ/kg-K, so that $h_v = 2500 + 1.82T$. The value 2500 is the specific enthalpy of the saturated steam at 0 Celsius.
- Air is modeled as an ideal gas of constant thermal capacity, $c_a = 1$ kJ/kg-K, so that $h_a = T$

In these approximations, the temperature T is in Celsius, and thermal capacities are values under constant pressure.

Thus, the specific enthalpy of moist air is

$h = T + \omega(2500 + 1.82T)$.

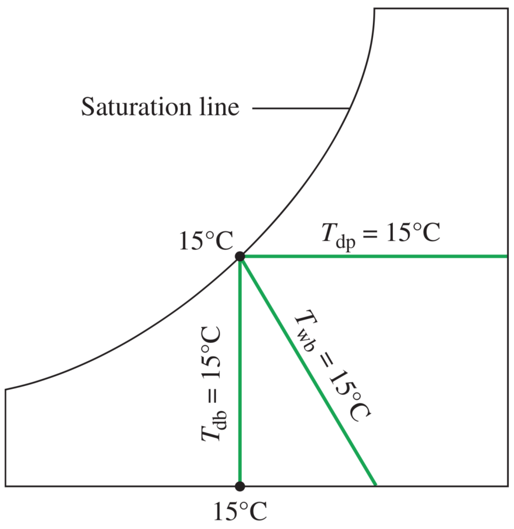
Here h is in the unit of kJ/kg, and T is in Celsius. Because of the enormous enthalpy of vaporization, 2500 kJ/kg, the contribution of the thermal capacity of water vapor, 1.82T, is negligible for practical range of temperature. The contribution of the thermal capacity of air, T, however, is significant, because ω is a small number.

On the T-ω plane, the lines of constant specific enthalpy are nearly straight lines.

Dew point temperature, T_{dew}. Define the dew point temperature, T_{dew}, by the equation

$P_v = P_g(T_{dew})$.

On the T-ω plane, the lines of constant dew point temperature are horizontal lines.



Psychrometric process

Heater.

Adiabatic saturation. YouTube adiabatic saturation temperature

Dehumidifier. YouTube dehumidifier.

Cooling tower. YouTube cooling tower 1, cooling tower 2.

Open system

Now enters another supporting role—the number of a species of molecules. In thermodynamics, the number of a species of molecules, energy, and volume play analogous supporting roles, of equal importance.

A family of isolated systems of many independent variables

An open system and its surroundings transfer energy, volume, and molecules. The molecules can be of many species. To illustrate the ideas, consider that only two species of molecules, 1 and 2, transfer between the open system and its surroundings. The open system may contain other species of molecules, but they are blocked from transfer between the open system and surroundings.

Of an open system, let the energy be U, volume be V, the number of molecules of species 1 be N_1, and the number of molecules of species 2 be N_2. When U, V, N_1, N_2 are fixed, the open system becomes an isolated system. Denote the number of quantum states of this isolated system by $\Omega(U,V, N_1, N_2)$. As U, V, N_1, N_2 vary, the function $\Omega(U,V,N_1,N_2)$, or its equivalent, $S(U,V,N_1,N_2) = \log \Omega(U,V,N_1,N_2)$, characterizes the open system as a *family* of isolated systems.

Definition of chemical potentials

For the function of four variables, $S(U,V,N_1,N_2)$, recall a fact of calculus:

$dS = (\partial S(U,V,N_1,N_2)/\partial U)dU + (\partial S(U,V,N_1,N_2)/\partial V)dV + (\partial S(U,V,N_1,N_2)/\partial N_1)dN_1 + (\partial S(U,V,N_1,N_2)/\partial N_2)dN_2$.

Between the open system and its surroundings, when we block the transfer of molecules, but allow the transfer of energy and volume, the open system becomes a closed system. We have already related two partial derivatives to thermodynamic properties:

$1/T = \partial S(U,V,N_1,N_2)/\partial U$, $P/T = \partial S(U,V,N_1,N_2)/\partial V$.

The other two partial derivatives define the *chemical potentials* (Gibbs, 1875):

$-\mu_1/T = \partial S(U,V,N_1,N_2)/\partial N_1$,
$-\mu_2/T = \partial S(U,V,N_1,N_2)/\partial N_2$.

The ratio μ_1/T is the child of the union of the entropy and the number of molecules of species 1, and the ratio μ_2/T is the child of the union of the entropy and the number of molecules of species 2, just as the temperature is the child of the union of entropy and energy, and as the ratio P/T is the child of the union of entropy and volume. The chemical potentials are intensive thermodynamic properties.

The unit for a chemical potential is energy per molecule. Often, the amount of molecules is measured in moles, so that the unit for a chemical potential is energy per mole. Occasionally, a chemical potential is reported in the unit of energy per mass. So, watch out for the unit used for a chemical potential.

Having defined the four partial derivatives in terms of thermodynamic properties, we now write

$dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$.

This equation applies to an open system, and generalizes the equation for a thermal system, and the equation for a closed system.

Temperature vs. chemical potential

Usage of words. When we speak of a chemical potential, we should identify both the molecular species and the open system. For example, we speak of the chemical potential of water molecules in a piece of cheese, or the chemical potential of water molecules in a glass of wine. We also speak of the chemical potential of carbon dioxide in a bottle of Coca Cola. Denote the chemical potential of molecular species 1 in open system A by $\mu_{1,A}$.

When we speak of temperature, we only need to identify the place. For example, we speak of the temperature of a piece of cheese, or the temperature of a glass of wine.

This difference in usage comes from something fundamental: our world has many species of molecules, but only one species of energy. The number of each species of molecules is conserved; for example, the number of oxygen molecules is conserved, and the number of nitrogen molecules is conserved. By contrast, all forms of energy can convert to one another: it is the total energy that is conserved.

Experimental significance of temperature. The temperature of a system measures the change in the entropy of the system associated with the change in energy. We measure temperature by using a thermometer, and adding energy to the system by using a heater. Energy flows from a place of high temperature to a place of low temperature. Temperature corresponds to the daily experience of hotness. Indeed, our daily experience of hotness is so pervasive that it may even impede our learning of thermodynamics. It takes significant effort for us to sort out, of all our feelings for hotness, what is essential and what is incidental. Only then we can link our daily experience of hotness to the thermodynamics of temperature.

Experimental significance of a chemical potential. The chemical potential of ethanol in a glass of wine measures the escaping tendency of ethanol from the wine. Ethanol goes from a place of high chemical potential to a place of low chemical potential. Chemical potential corresponds to the daily experience of the smell of the wine.

Of all species of molecules, water is particularly significant to us. Our parents do tell us about humidity. Indeed, our experience of humidity maps to the thermodynamics of the chemical potential of water, just as our experience of hotness maps to the thermodynamics of temperature.

In everyday language, some of us may say that a wine is concentrated with alcohol when we feel a strong smell. Indeed, we will show that the concentration of a solute in a solution maps to the chemical potential of the solute in the solution.

Why are we familiar with temperature, but not chemical potential? Given similarly pervasive roles of temperature and chemical potential in our lives, we may wonder why we do not have the same level of familiarity with the two quantities.

I can think of two reasons: cultural and technical. The cultural reason has to do with what our parents tell us. When we touch hot water, our parents tell us that the temperature of water is high. When we smell a strong wine, however, our parents miss the teachable moment, and fail to tell us that the chemical potential of ethanol is high. The phrase—the chemical potential of ethanol—is simply not in the everyday language. So blame our parents.

The technical reason is that, when we feel that something is hot, we attribute the sense of hotness to a single quantity: temperature. However, when we smell something, we may sense multiple quantities: a list of chemical potentials of a list of species of molecules. It is simpler to deal with one quantity than deal with multiple quantities. So blame our world: it confuses us with too many species of molecules.

BAT on two open systems in contact

Two open systems, A and B, are said to be in contact if they exchange energy, volume, and matter. We next analyze the two open systems in contact using the basic algorithm of thermodynamics (BAT).

Step 1. Construct an isolated system with internal variables. We characterize system A by a function $S_A(U_A,V_A,N_{1,A},N_{2,A})$, and system B by another function $S_B(U_B,V_B,N_{1,B},N_{2,B})$. Note that $N_{1,A}$ denotes the number of molecules of species 1 in system A. We make the composite of the two open systems into an isolated system. The principles of conservation require that

$U_A + U_B =$ constant,
$V_A + V_B =$ constant,
$N_{1,A} + N_{1,B} =$ constant,
$N_{2,A} + N_{2,B} =$ constant.

Here we assume that the two species of molecules do not undergo a chemical reaction, so that the number of molecules in each species is conserved. The composite is an isolated system of four independent internal variables: U_A, V_A, $N_{1,A}$, $N_{2,A}$.

Changes of the internal variables satisfy the following relations:

$dU_A + dU_B = 0$,
$dV_A + dV_B = 0$,
$dN_{1,A} + dN_{1,B} = 0$,
$dN_{2,A} + dN_{2,B} = 0$.

Step 2. Calculate the subset entropy of the isolated system as a function of the internal variables. When the independent internal variables $U_A,V_A,N_{1,A},N_{2,A}$ are fixed at particular values, the isolated system flips in a subset of the sample space. Denote the subset entropy by $S_{composite}(U_A,V_A,N_{1,A},N_{2,A})$. Entropy is an extensive quantity, so that the subset entropy is a sum:

$S_{composite}(U_A,V_A,N_{1,A},N_{2,A}) = S_A(U_A,V_A,N_{1,A},N_{2,A}) + S_B(U_B,V_B,N_{1,B},N_{2,B})$.

When the internal variables change by dU_A, dV_A, $dN_{1,A}$, $dN_{1,B}$, the subset entropy changes by

$dS_{composite} = (1/T_A - 1/T_B)dU_A + (P_A/T_A - P_B/T_B)dV_A + (- \mu_{1,A}/T_A + \mu_{1,B}/T_B)dN_{1,A} + (- \mu_{2,A}/T_A + \mu_{2,B}/T_B)dN_{2,A}$.

Step 3. Maximize the subset entropy to reach equilibrium. The four internal variables $U_A,V_A,N_{1,A},N_{2,A}$ can change independently. In equilibrium, the subset entropy maximizes, $dS_{composite} = 0$, so that

$T_A = T_B$,
$P_A = P_B$,
$\mu_{1,A} = \mu_{1,B}$,
$\mu_{2,A} = \mu_{2,B}$.

Equilibrium requires four conditions. The two open systems have the equal temperature, equal pressure, equal chemical potential of molecular species 1, and equal chemical potential of molecular species 2.

Step 4. Change the internal variable to increase the subset entropy; irreversibility. Out of equilibrium, the BAT requires that the subset entropy should increase as time progresses, $dS_{composite} > 0$.

Consider a situation where the two open systems are in partial equilibrium, $T_A = T_B$, $P_A = P_B$, $\mu_{1,A} = \mu_{1,B}$, but not in equilibrium with respect to the transfer of molecular species 2. The inequality $dS_{composite} > 0$ reduces to

$(- \mu_{2,A} + \mu_{2,B})dN_{2,A} > 0$.

Thus, molecular species 2 transfers from the system of high chemical potential to the system of low chemical potential. The presence of the negative sign in the definition of chemical potential leads to this verbal convenience. The chemical potential of a molecular species in an open system measure the escaping tendency of the species from the system.

The BAT keeps track of energy, volume, and matter, and never need the hair-splitting definition of heat and work. Indeed, defining heat and work for an open system is more convoluted than that for a closed system. We will never need such convoluted notion.

Experimental determination of the chemical potential of a species of molecules in an open system

How do we experimentally measure the chemical potential of a species of molecules in an open system? When two systems can exchange energy and a species of molecules, the fundamental postulate dictates that the two systems reach equilibrium when they have the same temperature and the same chemical potential of the species of molecules. Consequently, once the chemical potential of a species of molecules in one system is determined as a function of measurable properties, the system can be used to determine the chemical potential of the same species of molecules in other systems.

For example, we will show that the chemical potential of H_2O in pure H_2O coincides with the Gibbs function per molecule:

$\mu_{\text{H2O in pure H2O}} = h - Ts$.

The chemical potential of H_2O in pure H_2O is a function of temperature T and pressure P. The function is determined using enthalpy and entropy listed in steam tables, updated using references to be discussed later.

Now let us measure the chemical potential of H_2O in an arbitrary open system, such as a bottle of wine. We can bring the bottle of wine into contact with a flask of pure water vapor. The contact is made with a semipermeable membrane that allows H_2O molecules to go through, but blocks all other species of molecules. When the wine in the bottle equilibrates with the vapor in the flask, the two systems have the same temperature and the same chemical potential of H_2O. A reading of the temperature and pressure in the flask determines the chemical potential of H_2O in the flask, which is the same as the chemical potential of H_2O in the wine.

No litter

Littered in literature are quantities directly related to chemical potentials. Examples include fugacity, activity, water potential, and affinity. They add no value, and should not be used. If you have to read papers that contain these quantities, simply look up their definitions in Wikipedia and convert them back to chemical potentials.

Molecular reservoir

A molecular reservoir has a fixed chemical potential of a species of molecules, μ. For example, a large tank of an aqueous solution of salt is a molecular reservoir of H_2O. A small amount of H_2O molecules can go in and out of the tank, though the vapor. The salt evaporates negligibly. The chemical potential of H_2O in the solution is fixed.

Now consider an open system and a molecular reservoir. We can fix the chemical potential of a species of molecules in the open system by letting it transfer the species of molecules to the molecular reservoir. The situation is analogous to fixing temperature of a thermal system by letting it transfer energy with a thermal reservoir.

Next consider an open system in contact with a thermal reservoir of temperature T and a molecular reservoir of chemical potential μ_1 of species 1. Analogous to the Gibbs function, define

$L = U - TS + \mu_1 N_1$.

Recall that $dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$. The above definition gives that

$dL = -SdT + PdV - N_1 d\mu_1 + \mu_2 dN_2$.

Now we regard L as a function of four independent variables, $L(T, V, \mu_1, N_2)$, and relate its partial derivatives to thermodynamic properties.

The open system may have an internal variable x. The composite of the open system, the thermal reservoir, and the molecular reservoir constitutes an isolated system. As x changes, the isolated system reaches equilibrium when the function $L(x, T, V, \mu_1, N_2)$ minimizes.

Gibbs function

Recall the Gibbs function:

$G = U - TS + PV$.

Energy U is a relative property, and T, S, P, and V are absolute properties. The same additive constant appears in U also appears in the Gibbs function.

The definition of the Gibbs function, along with the equation $dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$, gives that

$dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2$.

This equation suggests that the Gibbs function be regarded as a function $G(T,P,N_1,N_2)$, with the partial derivatives

$-S = \partial G(T,P,N_1,N_2)/\partial T$,
$V = \partial G(T,P,N_1,N_2)/\partial P$,
$\mu_1 = \partial G(T,P,N_1,N_2)/\partial N_1$,
$\mu_2 = \partial G(T,P,N_1,N_2)/\partial N_2$.

Once the Gibbs function $G(T,P,N_1,N_2)$ is known, the above equations calculates the other functions: $S(T,P,N_1,N_2)$, $V(T,P,N_1,N_2)$, $\mu_1(T,P,N_1,N_2)$, $\mu_2(T,P,N_1,N_2)$.

Exercise. In an open system of two species of molecules, let the numbers of molecules of the two species be N_1 and N_2, the number fraction of species 1 be $y_1 = N_1/(N_1 + N_2)$, and the Gibbs function per molecule be $g = G/(N_1 + N_2)$. The Gibbs function per molecule is a function of three variables, $g(T,P,y_1)$. Given the function $g(T,P,y_1)$, calculate $\mu_1(T,P,y_1)$ and $\mu_2(T,P,y_1)$. For fixed T and P, interpret your results graphically on the g-y_1 plane.

Exercise. Define the Helmholtz function by $F = U - TS$. Show that $\mu_1 = \partial F(T,V,N_1,N_2)/\partial N_1$.

Mathematical relations

Once the chemical potentials are defined, we can derive many mathematical relations. These mathematical relations are inessential for understanding and application of thermodynamics, but may bring occasional convenience. I will not spend much time on such relations, but will give a few examples.

Homogeneous function in calculus. Let $Z(X,Y)$ be a function. The results below readily generalize to a function of any number of independent variables. Denote $a = \partial Z(X,Y)/\partial X$ and $b = \partial Z(X,Y)/\partial Y$. Recall a fact of calculus: $dZ = adX + bdY$.

A function $Z(X,Y)$ is called a *homogeneous function* if, for any number λ, the following relation holds:

$\lambda Z(X,Y) = Z(\lambda X,\lambda Y)$.

For a homogeneous function, $Z(X,Y)$, when X, Y and Z are multiplied by a number λ, the two slopes, a and b, do not change. Thus, we can write $dZ = adX + bdY$ as $d(\lambda Z) = ad(\lambda X) + bd(\lambda Y)$. Recall that $d(\lambda Z) = Zd\lambda + \lambda dZ$, $d(\lambda X) = Xd\lambda + \lambda dX$, and $d(\lambda Y) = Yd\lambda + \lambda dY$. The equation $d(\lambda Z) = ad(\lambda X) + bd(\lambda Y)$ becomes that

$Z = aX + bY$.

This equation is called the *Euler relation.*

Taking derivative of the Euler equation, we obtain that $dZ = adX + Xda + bdY + Ydb$. This equation, along with $dZ = adX + bdY$, gives that

$Xda + Ydb = 0$.

This equation is called the *Gibbs-Duhem relation*.

Homogeneous function in thermodynamics. We next apply these mathematical relations to an open system of two species of molecules, characterized by the function $S(U,V,N_1,N_2)$. Recall that

$dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$.

This equation identifies the four partial derivatives of the function $S(U,V,N_1,N_2)$. The function $S(U,V,N_1,N_2)$ involves five extensive properties, and is a homogeneous function. The four partial derivatives of the function define the four intensive properties. When we multiply every extensive property by a number λ, the open system increases size proportionally, but all the intensive properties remain unchanged.

The Euler relation for the homogeneous function $S(U,V,N_1,N_2)$ is

$S = U/T + PV/T - N_1\mu_1/T - N_2\mu_2/T$.

This equation, along with the definition of the Gibbs function, $G = U - TS + PV$, gives an identity:

$G = \mu_1 N_1 + \mu_2 N_2$.

For the open system, invert the function $S(U,V,N_1,N_2)$ to obtain the function $U(S,V,N_1,N_2)$, which is also a homogeneous function. From $dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$ we obtain that

$dU = TdS - PdV + \mu_1 dN_1 + \mu_2 dN_2$.

This equation identifies the four partial derivatives of the function $U(S,V,N_1,N_2)$. The Gibbs-Duhem relation for the function $U(S,V,N_1,N_2)$ is

$SdT - VdP + N_1 d\mu_1 + N_2 d\mu_2 = 0$.

Chemical potentials of molecules in simple systems

The onerous task of collecting big data

Given an open system of two molecular species, the chemical potentials of the two species in the open system are two functions of three variables, $\mu_1(T,P,y_1)$ and $\mu_2(T,P,y_1)$. A function of three variables will be time-consuming to determine experimentally. The task becomes even more onerous for a system of more species of molecules. Despite persistent attempts since Gibbs defined chemical potentials (1875), the general problem remains challenging.

We next give chemical potentials of molecules in a few simple systems:

- Pure substance
- Incompressible pure substance

- Pure ideal gas
- Ideal gas mixture

Pure substance

We now consider the chemical potential of molecules in a pure substance.

Chemical potential is an intensive property. A state of a pure substance is specified by two intensive properties, temperature and pressure. Thus, for a pure substance, the three intensive properties, chemical potential, temperature, and pressure, are not independent properties. We now derive a relation between them.

We model a piece of a pure substance as an open system of a characteristic function S(U,V,N). Thus,

$dS = (1/T)dU + (P/T)dV - (\mu/T)dN$

This equation defines the temperature T, pressure P, and chemical potential μ.

We can increase the number of molecules the piece without changing the functions of state per molecule, u, v, s, and without changing T and P. When we add dN number of molecules to the piece, the extensive functions of state change by $dS = sdN$, $dU = udN$, and $dV = vdN$. The equation $dS = (1/T)dU + (P/T)dV - (\mu/T)dN$ becomes

$s = (1/T)u + (P/T)v - (\mu/T)$.

Rearranging, we find that

$\mu = u + Pv - Ts$.

This equation shows that the chemical potential of molecules in a pure substance equals the Gibbs function per molecule.

Chemical potential of molecules is the same in every phase in a mixture of phases in equilibrium. Recall the theory of pure substance. When two or three phases are in equilibrium, the chemical potential of molecules is the same in every phase. Thus, when a state water is in equilibrium with a state of steam,

$\mu_{water} = \mu_{steam}$.

When a state of water, a state of ice, and a state of steam equilibrate,

$\mu_{water} = \mu_{ice} = \mu_{steam}$.

Chemical potential is a relative property. Of the five quantities on the right-hand side of the above equation, only energy u has an arbitrary additive constant. The same additive constant appears in the chemical potential of the molecular species in the pure substance. We will say more about this additive constant when we use chemical potentials in a chemical reaction.

By convention, most steam tables set the entropy to be zero for water in water-ice-steam equilibrium, and list entropy in other states relative to this state of water. The absolute entropy is 3.519 kJ/Kg-K for water in water-ice-steam equilibrium. We should add this value to each entropy in the steam tables to obtain the absolute entropy for every state of H_2O.

Chemical potential is a function of temperature and pressure. Recall that $ds = (1/T)du + (P/T)dv$. This equation, along with $\mu = u + Pv - Ts$, gives that

$$d\mu = - sdT + vdP.$$

This equation suggests that we regard the chemical potential as a function of temperature and pressure, $\mu(T,P)$, with the partial derivatives

$$\partial\mu(T,P)/\partial T = - s, \quad \partial\mu(T,P)/\partial P = v.$$

These results recover the similar equations when we regard the chemical potential of a species of molecules in a pure substance as the Gibbs function per molecule of the substance.

Incompressible pure substance

In many applications of liquids and solids, the pressure is small, so that the volume per molecule in the system v, is taken to be independent of the pressure, and the system is called *incompressible*.

Recall the chemical potential of a species of molecules in a pure substance, $\mu = u + Pv - Ts$. For an incompressible substance, u, v, and s are functions of T, and are independent of P. Let P_0 be a reference pressure. Write

$$\mu(T,P) = \mu(T,P_0) + (P - P_0)v(T).$$

At a fixed temperature, the chemical potential of a species of molecules in an incompressible liquid is linear in pressure.

Pure ideal gas

An ideal gas, of N number of a single species of molecules in a flask of volume V, is subject to pressure P and temperature T. Recall the equations of states:

$PV = Nk_BT.$
$dU = Nc_V(T)dT$
$dH = Nc_P(T)dT,\ c_P(T) = c_V(T) + k_B$
$dS = (Nc_P(T)/T)dT - (Nk_B/P)dP$

For many species of molecules, the functions $h(T)$ and $s(T, P_0)$ are tabulated. Here P_0 is an arbitrary pressure. Recall that $s(T, P) = s(T, P_0) - k_B \log(P/P_0)$. The reference $s(T, P_0)$ is available for many species of molecules. The chemical potential $\mu = u + Pv - Ts$ can be written as

$\mu(T,P) = \mu(T,P_0) + k_BT \log(P/P_0),$

where the reference is

$\mu(T,P_0) = h(T) - Ts(T,P_0).$

Thus, the function $\mu(T,P)$ is a relative property, and has the same arbitrary constant as that for h. The two functions, $h(T)$ and $s(T,P_0)$, are listed in the ideal gas tables for various species of molecules.

Ideal gas mixture

The chemical potential of molecules of species 1 in an ideal gas mixture is

$\mu_1(T,P_1) = \mu_1(T,P_0) + k_BT \log(P_1/P_0),$

where P_1 is the partial pressure of species 1 in the mixture, and the reference is

$\mu_1(T,P_0) = h_1(T) - Ts_1(T,P_0).$

This reference is the same for a pure ideal gas, and is available for many species of molecules. Thus, to determine the chemical potential of a species of molecules in an ideal gas mixture, we just measure the partial pressure of the species in the mixture.

Electronic nose

Humans smell alcohol but not water. Dogs may have better sense of smell than humans for many species of molecules. An active field of research is to develop electronic noses to detect trace amounts of molecules in the air.

Given an open system, every species of molecules in the system will release a vapor into the surrounding air. The mixture of the vapors of all species of molecules—to a good approximation—is an ideal gas. By measuring the partial pressure of a species of molecules in the surrounding air, we determine the chemical potential of the species in the air, which equals the chemical potential of the species in the open system, or at least in part of the open system near the surface. That is, the electronic nose can smell the content of the open system.

Relative humidity

At a given temperature, when a moist air is in equilibrium with the liquid water, we say that the air is saturated with water. If air contains fewer water molecules than the saturated air does, the number of water molecules in the air divided by the number of water molecules in the saturated air is called the relative humidity. Write

$RH = N/N_{satu}$.

When the vapor is modeled as an ideal gas, the relative humidity is also given by

$RH = P/P_{satu}$,

where P is the partial pressure of H_2O in the unsaturated gas, $P < P_{satu}$.

Write the chemical potential of water in the air as

$\mu(T,P) = \mu(T,P_{satu}) + k_BT \log(P/P_{satu})$.

The chemical potential of H_2O in moist air relates to the relative humidity. Our parents are not totally negligent. They do mention humidity.

The lung is always saturated with water vapor at the body temperature (37C), but the atmospheric air may not be. In winter, the cold air outside has low water content even at 100% relative humidity. When the cold air enters a warm room, the relative humidity in the room will reduce below 100% at room temperature. We will feel uncomfortable. Also, water inside the warm room will condense on cold window panes.

The ascent of sap

The cost of an invasion

Youtube Ascent of sap, Xylem, Stomata. Plants photosynthesize sugar from water and carbon dioxide. In the beginning, all plants lived under water, and almost all parts of a plant engage in photosynthesis.

Then some plants emerged from water and invaded the land. They had to evolve body parts to divide the labor of photosynthesis. Consider a tree. The leaves acquire light from the sun, and carbon dioxide from the air. The roots acquire water from the ground. The trunk takes the leaves to a height unshadowed by other plants, and transports water from the roots to the leaves.

Transpiration pulls liquid water up

How does a tree transport liquid water from the roots to the leaves, sometimes 100 meters tall? This ancient question was answered by Dixon and Joly (1895). Unlike an animal, the tree does not have a heart to pump liquid. The tree does have a system of tubes, called *xylem*, to conduct liquid water. The humidity in the ground is high, perhaps saturated with water. The humidity in the air is low, especially in the dry weather. This difference in humidity pumps water molecules up. Outside the tree, water molecules ascend as vapor. Inside the tree, water molecules ascend as liquid.

At the top of the tree, the chemical potential of H_2O molecules in the liquid inside the tree is linear in the pressure. Write

$\mu(T,P_{top}) = \mu(T,P_{satu}) + (P_{top} - P_{satu})v$.

The chemical potential of H_2O molecules in the moist air is

$\mu(T,P_v) = \mu(T,P_{satu}) + k_BT \log(P_v/P_{satu})$,

where P_v is the partial pressure of H_2O in the air.

When the liquid H_2O in the tree equilibrates with the gaseous H_2O in the air, the two chemical potentials are equal, so that

$P_{top} - P_{satu} = (k_BT/v) \log (P_v/P_{satu})$.

The specific volume of liquid H_2O is 10^{-3} m^3/kg. 1 Mole of H_2O has a mass of 18 grams. The mass per mole of water The volume per molecule in liquid H_2O is $v = (10^{-3}\ m^3/kg)$ (18 g/mol)/(6.022×10^{23}/mol) = $3 \times 10^{-29}\ m^3$. At temperature T = 300K, $k_BT = (1.38 \times 10^{-23}\ J/K)(300\ K) = 4.14 \times 10^{-21}$ J. Thus,

k_BT/v = 138 MPa.

This prefactor is enormous: even a high humidity will generate large tensile stress. At a relative humidity of P_v/P_{satu} = 90%, the pressure in liquid water is $P_{top} - P_{satu}$ = - 14.5 MPa. At a relative humidity of P_v/P_{satu} = 80%, the pressure in liquid water is $P_{top} - P_{satu}$ = - 30.8 MPa. At a relative humidity of P_v/P_{satu} = 50%, the pressure in liquid water is $P_{top} - P_{satu}$ = - 95.7 MPa. The low humidity in the air can cause enormous tensile stress in the liquid water in the xylems.

The tensile stress in xylem at the top of a tree

Let us view a column of water as a free body. Let A be the cross-sectional area of the column. The pressure in the water at the top of the tree, P_{top}, exerts a force AP_{top}. The pressure in the water at the bottom of the tree, P_{bottom}, exerts a force AP_{bottom}. The column of water weighs ρghA, where ρ is the mass density of water, g is the acceleration of gravity, and h is the height of the tree. The balance of the three forces requires that

$P_{top} = P_{bottom} - \rho gh$.

At the bottom of the tree, water in the tree equilibrates with water in the soil, taken to be saturated, $P_{bottom} = P_{satu}$. At 300 K, P_{satu} = 3 kPa. For a 100 m tall tree, $\rho gh = (1000\ kg/m^3)(10\ m/s^2)(100\ m) = 1$ MPa. Thus, the pressure in the water at the top of the tree is enormous and negative. A negative pressure means a tensile stress. Thus, in the xylem, the water is lifted by a tensile stress acting at the top of the tree.

A tree is a microfluidic device. Gravity pulls the liquid water down, and transpiration pulls the liquid water up. Liquid water in the xylems at the top of the tree is under tension. The column of water sustains the tension without rupture by the hydrogen bonds between water molecules. In drought, the enormous tensile stress ruptures the liquid water in the xylems, and the tree dies.

In the above calculation, we have neglected the atmospheric pressure (100 kPa) due to nitrogen and oxygen in the air. The same atmospheric pressure acts everywhere and does not affect the ascent of sap.

Exercise. To mimic the transpiration pull in a tree, consider a drop of water confined in a hydrogel. The hydrogel aggregates a polymer network and water molecules, and water molecules can permeate through the hydrogel. When the relative humidity in the surrounding air is 85%, determine the stress in the drop of water in equilibrium.

Exercise. Wiki osmotic power. Describe the working principle.

BAT on a tree

Let us run the basic algorithm of thermodynamics on a tree.

Step 1. Construct an isolated system with internal variables. An isolated system consists of four parts: the tree, the inlet (i.e., the soil surrounding the roots), the exit (i.e., the air surrounding the leaves), and a thermal reservoir (i.e., the environment of temperature T). Assume that the ascent of sap is a steady flow, so that the tree does not change energy. The conservation of energy requires that

$- h_i + h_e + gZ + q = 0$.

All quantities are per unit mass. The exit is at the height of the tree, Z. The tree transfers energy by heat q to the environment.

Step 2. Calculate the entropy generation of the isolated system.

$s_{gen} = - s_i + s_e + q/T$.

Eliminating q from the above two equations, we obtain that

$s_{gen} = (h_i/T - s_i) - (h_e/T - s_e) - gZ/T$.

Step 3. A reversible process generates no entropy. Set $s_{gen} = 0$, and we obtain that

$gZ_{rev} = (h_i - Ts_i) - (h_e - Ts_e)$.

Here Z_{rev} stands for the height achieved by a reversible process. The right side is the difference in chemical potential between the inlet and exit. At the inlet, the chemical potential of H_2O in the soil equals the chemical potential in the air nearby. Let P_i be the partial pressure of H_2O at the inlet. Thus, the chemical potential of H_2O at the inlet is

$h_i - Ts_i = \mu(T,P_{satu}) + R_{H2O}T \log(P_i/P_{satu})$.

Here $R_{H2O} = 0.46$ kJ/kg-K is the specific gas constant for H_2O. Similarly, the chemical potential of H_2O at the exit is

$h_e - Ts_e = \mu(T,P_{satu}) + R_{H2O}T \log(P_e/P_{satu})$.

Insert the two chemical potentials into the equation for gh_{rev}, and we obtain that

$gZ_{rev} = R_{H2O}T \log(P_i/P_e)$.

The ascent by a reversible process, h_{rev}, is set by the ratio of the partial pressure of H_2O vapor at the roots and leaves. At $P_i/P_e = 2$ and $T = 300$ K,

$Z_{rev} = (10 \text{ m/s}^2)^{-1}(0.46 \times 10^3 \text{ J/kg-K})(300 \text{ K}) \log 2 = 9357$ m.

A difference in relative humidity is indeed a powerful pump! A value of $P_i/P_e = 2$ corresponds to, for example, roots in soil saturated with water, and leaves in air at a relative humidity of 50%.

Step 4. An actual process is irreversible, and generates entropy. Set $s_{gen} > 0$, and we obtain that $Z < Z_{rev}$. The actual ascent of a tree is less than the ascent by a reversible process.

The second-law efficiency of a tree is Z/Z_{rev}. Even a 100 m tall tree has an extremely low second-law efficiency, about 1%. A tree is an inefficient pump created by the Nature. What a wasteful Nature! Will an engineer do better?

As usual, the BAT says neither how to achieve the reversible process nor what causes irreversibility. But we know obvious suspects. The ascent of sap need overcome viscosity and maintain cohesion.

(By Maxwell Urbani, Harvard ‘21)

Chemical reaction

Conservation of matter

A chemical reaction conserves matter in the following sense. The reaction breaks one set of molecules, called *reactants*, and forms another set of molecules, called *products*. The reaction changes the number of each species of molecules, but conserves the number of each species of atoms.

Chemical equation. A chemical reaction is represented by a chemical equation. Look at a chemical equation:

$H_2 + 0.5O_2 = H_2O$.

The equation places the reactants on the left, and the products on the right. Each term is the chemical formula of a molecule, with a number placed in front.

Chemical formula. This particular reaction involves three species of molecules: hydrogen H_2, oxygen O_2, and water H_2O. A hydrogen molecule consists of two hydrogen atoms, an oxygen molecule consists of two oxygen atoms, and a water molecule consists of two hydrogen atoms and one oxygen atom. The chemical formula of a molecule shows the species and numbers of atoms that constitute the molecule.

Stoichiometric coefficient. The chemical equation ensures that every species of atoms is conserved by placing in front of each chemical formula a number, called the *stoichiometric coefficient*. The stoichiometric coefficients are determined by equating the numbers of every species of atoms on the two sides of the chemical equation.

Exercise. A reaction fundamental to life on Earth is photosynthesis. Plants absorb carbon dioxide and water to produce glucose. Determine the stoichiometric coefficients of the reaction.

Absolute entropy

From the tables of data, we find values of enthalpy and entropy of the three species of molecules at 25 Celsius, 100 kPa.

	h (J/mol)	s (J/mol-K)
H_2	0	130.678
O_2	0	205.148
H_2O (gas)	-241826	188.834
H_2O (liquid)	-285830	69.960

Entropy is an absolute property. Relative entropy is used only in applications that involve only difference in entropies of different states. In analyzing chemical reactions, we use absolute entropy, not relative entropy. All entropies listed in the table above are absolute entropies. Relative entropy is a needless complication, and should have never been introduced in the first place.

Unfortunately, steam tables commonly list relative entropies, setting zero entropy for water in water-ice-steam equilibrium. The absolute entropy of water in water-ice-steam equilibrium is 3.519 kJ/kg-K. Thus, we update the steam tables by adding 3.519 kJ/kg-K to each entry of entropy in to obtain the absolute entropy of every state of H_2O.

Conservation of energy

Recall the definition of enthalpy, h = u + Pv. Note that P and v are absolute properties, but u is a relative property, so that h is also a relative property. What is the reference for enthalpy?

Ideal gas tables. At 25 Celsius and 100 kPa, H_2O molecules form a liquid. The enthalpy of H_2O (gas) listed in the above table is the hypothetical ideal-gas enthalpy. Table A.9 lists values of h(T) - h(25 C). That is, the table lists enthalpy as a function of temperature, using h(25 C) as a reference. At a temperature where H_2O molecules form an ideal gas, Table A.9 gives the enthalpy.

Steam tables. At 25 Celsius, 100 kPa, the table above lists the enthalpy of H_2O (liquid) as

-285830 J/mol = -(285830 J/mol)/(18 g/mol) = -15879.44 J/g,

but the NIST steam tables list the enthalpy as + 104.92 J/g. The two values of enthalpy differ in both magnitude and sign. What happens?

Enthalpy of reaction. Represent a steady-state reactor as a control volume. The inlet comes with a stream of H_2 at a rate of 1 mole per unit time, and a steam of O_2 at a rate of 0.5 mole per unit time. The exit leaves with a steam of HO_2 (liquid) at a rate of 1 mole per unit time. All three streams are at 25 Celsius, 100 kPa. Let q be the energy transfer by heat, taken to be positive when energy transfers from the surroundings to the reactor.

The conservation of energy requires that

$h_{HO2} = h_{H2} + 0.5\ h_{O2} + q.$

Such an experiment gives the value q = -285830 J/mol. The negative sign means that the reaction transfers energy from the reactor to the surroundings. By convention, we set $h_{H2} = 0$ and $h_{O2} = 0$ at 25 Celsius, 100 kPa. The experiment then gives $h_{HO2} = -285830$ J/mol at 25 Celsius, 100 kPa. The chemical reaction does not allow us to assign an arbitrary reference enthalpy of H_2O. However, steam tables commonly set zero enthalpy for the state of water in water-ice-steam equilibrium.

Update the enthalpies in steam stables for chemical reaction. At 25 Celsius, 100 kPa, the steam tables list the enthalpy of water at 104.92 J/g. The difference of the two values is

-15879.44 J/g - 104.92 J/g = - 15984.36 J/g.

This value gives the enthalpy of the state of water at the water-ice-steam equilibrium. Update the steam stables by adding this value to each entry of enthalpy. The enthalpy so updated is suitable in analyzing chemical reactions.

Exercise. In a steady-state reaction, 1 mole of hydrogen enters the reactor at 25 Celsius, 100 kPa, 0.5 mole of oxygen enters the reactor at 25 Celsius, 100 kPa, and 1 mole of water exits the reactor at 200 Celsius, 1 MPa. Update steam stables to determine the enthalpy of reaction.

Exercise. In a steady-state reaction, 1 mole of hydrogen enters the reactor at 25 Celsius, 100 kPa, 0.5 mole of oxygen enters the reactor at 25 Celsius, 100 kPa, and 1 mole of ice exits the reactor at - 50 Celsius. Determine the enthalpy of reaction. Recall that the specific thermal capacity for ice is 2.06 kJ/kg-K, and the specific thermal capacity for water is 4.18 kJ/kg-K.

Exercise. Set the enthalpy of O_2 to be zero at 25 Celsius, 100 kPa. Find the specific enthalpy of O_2 at 100 Celsius, 1 MPa.

Change of enthalpy in several processes

Enthalpy of formation. The value -285830 J/mol is called the *standard enthalpy of formation*. The word “standard” means each of the reactant and product in the reaction enters or leaves the reactor in a standard state, commonly set at 25 Celsius, 100 kPa. The molar mass of water is 18 g/mol, so that the enthalpy of formation is (-285830 J/mol)/(18 g/mol) = - 15879 J/g.

Enthalpy of vaporization. We have long learned from steam tables that the change of enthalpy due to change of phase from water to steam at zero Celsius is about 2500 J/g.

Change of enthalpy due to change in temperature. When the temperature of water is increased by 1 Celsius, the enthalpy of water changes by 4.18 J/g.

These enormously different changes of enthalpy reflect different molecular processes. In reaction, molecules break and reform covalent bonds. In evaporation, water molecules break hydrogen bonds. In increasing temperature, water molecules vibrate more.

BAT on a reaction

We now run the basic algorithm of thermodynamics on the reaction $H_2 + 0.5O_2 = H_2O$.

Step 1. Identify an isolated system with internal variables. Represent a steady-state reactor as a control volume. The inlet comes with a stream of H_2 at a rate of 1 mole per unit time, and a steam of O_2 at a rate of 0.5 mole per unit time. The exit leaves with a steam of HO_2 (liquid) at a rate of 1 mole per unit time. In this analysis, to be general, we allow each stream to have its own temperature and pressure. Let q_0 be the energy transfer by heat from the reactor to the environment of fixed temperature T_0. Let w be the work produced by the reaction.

The isolated system has six parts: the reactor, the three streams, the environment, and the work-producing device. The stoichiometric coefficients ensure that the isolated system conserves each species of atoms. The isolated system conserves energy:

$- h_{H2} - 0.5\, h_{O2} + h_{H2O} + q_0 + w = 0.$

The steady-state reactor does not change energy.

Step 2. Find the entropy generation of the isolated system.

$s_{gen} = - s_{H2} - 0.5\, s_{O2} + s_{H2O} + q_0/T_0.$

The steady-state reactor does not change entropy. Nor does the work-producing device.

Eliminate q_0 from the above two equations, and we obtain that

$s_{gen} = (- s_{H2} - 0.5\, s_{O2} + s_{H2O}) + (h_{H2} + 0.5\, h_{O2} - h_{H2O})/T_0 - w/T_0.$

Step 3. A reversible process of the isolated system generates no entropy. Set $s_{gen} = 0$, and we obtain the reversible work:

$w_{rev} = (h_{H2} + 0.5\, h_{O2} - h_{H2O}) + T_0(- s_{H2} - 0.5\, s_{O2} + s_{H2O}).$

Step 4. An irreversible process of the isolated system generates entropy. Set $s_{gen} > 0$, and we obtain that

$w < w_{res}.$

The actual work generated by the reaction is below the reversible work. The second-law efficiency is w/w_{res}.

Enthalpy-entropy conflict

The expression for w_{rev} involves three streams of molecules, each having its own temperature and pressure. The environment is at yet another temperature T_0.

Now consider a special case, in which all three streams have the same pressure P and the same temperature T. Also set the temperature of the environment to be T. Thus,

$w_{rev} = \mu_{H2} + 0.5\, \mu_{O2} - \mu_{H2O}.$

The chemical potential of each species is at the state of T and P. The coefficients in front of the chemical potentials are the stoichiometric coefficients of the reaction.

Further specialize the state to T = 25 Celsius and P = 100 kPa. That is, each stream of molecules is in the standard state. The enthalpy of reaction is

$\Delta h = h_{H2} + 0.5\ h_{O2} - h_{H2O}$ = - 285830 J/mol - 0 - 0 = - 285830 J/mol.

The entropy of reaction is

$\Delta s = s_{H2} + 0.5\ s_{O2} - s_{H2O}$ = 69.960 J/mol-K - 130.678 J/mol-K - 0.5(205.148) J/mol-K = -163.292 J/mol-K.

The reversible work is

$w_{rev} = - \Delta h + T\Delta s$ = 285830 J/mol - (298 K)(163.292 J/mol-K) = 237168 J/mol.

In this example, when all streams of molecules are in the standard state, the reaction reduces both enthalpy and entropy. The former increases the reversible work, but the latter decreases the reversible work. Enthalpy and entropy are said to conflict. In this example, enthalpy prevails over entropy: the reaction produces reversible work. When hydrogen and oxygen react to form water, the net number of molecules reduces, so that the reaction reduces entropy. At an elevated temperature, the effect of entropy becomes more pronounced, and the reversible work reduces.

Exercise. In a steady-state reaction, 1 mole of hydrogen molecules enters the reactor at 100 Celsius, 100 kPa, 0.5 mole of oxygen enters the reactor at 100 Celsius, 100 kPa, and 1 mole of water exits the reactor at 200 Celsius, 1 MPa. Determine the reversible work, assuming an environment of 20 Celsius.

Fuel cell

Steady-state reaction. Let us look at the reaction again:

$H_2 + 0.5O_2 = H_2O$.

Assume that the reaction runs in a steady state. We have run the BAT on the reaction. The isolated system has six parts: the reactor, three streams of molecules, a thermal reservoir (i.e., environment), and a work-producing device. The conservation of energy requires that

$- h_{H2} - 0.5\ h_{O2} + h_{H2O} + q_0 + w = 0$.

The entropy generation is

$s_{gen} = - s_{H2} - 0.5\ s_{O2} + s_{H2O} + q_0/T_0$.

Of the six parts of the isolated system, the steady-state reactor and the work-producing device do not change entropy. The BAT requires that the isolated system undergo either a reversible process by keeping constant subset entropy, $s_{gen} = 0$, or an irreversible process by generating subset entropy, $s_{gen} > 0$.

As usual, the BAT tells us neither how to approach the reversible work, nor how irreversibility reduces the actual work. We have not even specified the mechanism of the work-producing device. The BAT is not the end, but a new beginning. Let us examine several experimental setups.

Isothermal reaction that produces heat but no work. When H_2 and O_2 react in a steady-state reactor to form H_2O, the reaction generates heat, but no work. For example, consider reaction at a constant temperature. That is, the inlet, exit, and environment have the same temperature T_0. The reaction does no work, $w = 0$, and the conservation of energy requires that

$q_0 = h_{H2} + 0.5\ h_{O2} - h_{H2O}$.

This energy transfers by heat from the reactor to the environment. The entropy generation becomes that

$s_{gen} = - s_{H2} - 0.5\ s_{O2} + s_{H2O} + (h_{H2} + 0.5\ h_{O2} - h_{H2O})/T_0$.

The isolated system includes the reactor, inlet, exit, work-producing device, and environment. The reactor runs in a steady state, and does not change entropy. The entropy generation includes terms from the three streams of molecules, as well as the environment.

Thermal engine. We can use the reaction to maintain a thermal reservoir of high temperature T, and operate a thermal engine between the thermal reservoir and a thermal reservoir of a low temperature T_0 (i.e., the environment). The engine produces work. This process converts the chemical energy to work indirectly, through thermal energy.

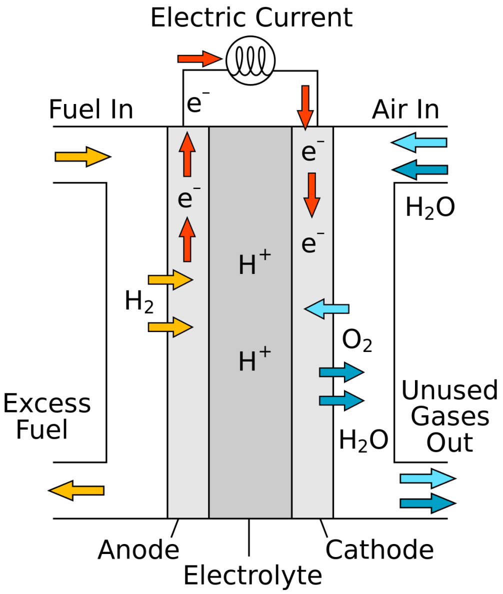
Electrochemistry. We next examine a specific work-producing device: a *fuel cell*. YouTube fuel cell. Wiki fuel cell. A fuel cell converts the chemical energy to work directly. In a fuel cell, H_2 and O_2 are separated by an electrolyte. The electrolyte lets the hydrogen ions H^+ go across, but not the hydrogen molecules H_2.

The electrolyte is sandwiched between two electrodes: an anode and a cathode. The two electrodes are connected through a resistor, such as a light bulb, via metal wires. At the anode/electrolyte interface, each H_2 molecule splits into two ions and two electrons:

$H_2 = 2H^+ + 2e^-$.

The hydrogen ions go through the electrolyte, while the electrons go through the metal wire and power the light bulb.

At the electrolyte/cathode interface, the hydrogen ions and the electrons react with oxygen to form water.



Electrical work. When the metal wires are connected with a resistor of resistance R, we measure a current I through the resistor, and voltage V across the resistor. When the reaction consumes 1 mole of H_2, the anode produces a number of electrons, $2N_Ae$, where N_A is the Avogadro constant, and the voltage V does electrical work

$w = 2N_AeV$.

Equilibrium. When we use a resistor of large resistance, the current through the resistor approaches zero, and the voltage across the resistor approaches an upper bound, called the *open-circuit voltage*, V_{open}.

As the current approaches zero, the reaction approaches equilibrium, and the electrical work approaches the reversible work, w_{rev}. In equilibrium, the reversible work equals the electrical work by the open-circuit voltage:

$w_{rev} = 2N_AeV_{open}$.

When the reaction $H_2 + 0.5O_2 = H_2O$ consumes 1 mole of H_2, the reversible work is $w_{rev} = 237168$ J/mol, and the open-circuit voltage is

$V_{open} = w_{rev}/(2N_Ae) = (237168 \text{ J/mol})/(2(6.022 \times 10^{23} \text{ mol}^{-1})(1.6 \times 10^{-19} \text{ coulombs})) = 1.2$ Volts.

The open-circuit voltage is achieved in equilibrium, when the current approaches zero, and the power IV approaches zero. That is, the reaction takes infinite time to consumes 1 mole of H_2 and produce the reversible work.

Irreversibility. At a finite electric current, the reaction is out of equilibrium, and produces irreversible processes, including reactions at the interfaces, the electron current through the metal wires, and the ion current through the electrolyte. These irreversible processes make the actual work smaller than the reversible work, $w < w_{rev}$, and make the actual voltage below the open-circuit voltage, $V < V_{open}$.

Exercise. Calculate the open-circuit voltage for a fuel cell that uses methane as the fuel.

Exercise. 1 mole of H_2 molecules and 0.5 mole of O_2 molecules enter a reactor, and 1 mole of H_2O molecules exit the reactor. Each of the three streams of molecules is in the state of 25 Celsius, 100 kPa. The reactor runs in a steady state, and is in thermal contact with an environment of 25 Celsius. Determine the energy transfer by heat from the reactor to the environment under each of the following assumptions:

A. Assume that the reactor is not connected to any work-producing device.
B. Assume that the reactor is connected to a work-producing device and the setup approaches equilibrium.
C. Assume that the reaction runs a fuel cell at a voltage of 1 V.

Lithium ion batteries

YouTube Announcement of the Nobel Prize in Chemistry 2019.

Exercise. Describe how a lithium ion battery works.

Theoretical air

In combustion, a fuel reacts with oxygen. But oxygen is commonly supplied by air, along with nitrogen and small amounts of other species of molecules. To a first approximation, nitrogen and other molecules do not participate in breaking or reforming molecules, but will change temperature during reaction.

As an idealization, model 1 mole of air as 0.79 mole of N_2 and 0.21 moles of O_2. The ratio of N_2 to O_2 is 0.79/0.21 = 3.76.

For the reaction $H_2 + 0.5O_2 = H_2O$, if we mix H_2 with air of the just right amount of O_2, the equation of reaction becomes

$H_2 + 0.5(O_2 + 3.76N_2) = H_2O + 1.88N_2$.

This amount of air is called the 100% *theoretical air* for this reaction.

Dew point

H_2 reacts with 400% theoretical air and results in a product having a pressure of 100 kPa. Determine the dew point of the product.

The chemical equation for this reaction is

$H_2 + 4x0.5(O_2 + 3.76N_2) = H_2O + 1.5O_2 + 7.52N_2$.

The mole fraction of H_2O in the product is

$y_{H2O} = 1/(1 + 1.5 + 7.52) = 0.1$.

The pressure of the product is P = 100 kPa. The partial pressure of H_2O in the product is

$P_{H2O} = y_{H2O}P = (0.1)(100 \text{ kPa}) = 10 \text{ kPa}$.

According to the NIST saturation (pressure) table, the pressure 10 kPa corresponds to a saturation temperature at about 45.8 Celsius, which is the dew point of the product.

Energy transfer by heat

Model a reactor as a control volume in steady state. The reactants enter the reactor from the inlet, and the products leave the reactor from the exit. In addition to the inlet and exit, the reactor and the surroundings transfer energy by heat, Q, taken to be positive if energy transfers from the surroundings to the reactor. This sign convention, along with the conservation of energy, requires that

$Q = H_{products} - H_{reactants}$.

Here $H_{products}$ is the enthalpy of the products, and $H_{reactants}$ is the enthalpy of the reactants.

Example.10 mole of H_2 and 200% theoretical air enter a steady-state reactor at 500 K, and the products exit the reactor at 1000 K. Determine the energy transfer by heat.

The chemical equation is

$H_2 + 2x0.5(O_2 + 3.76N_2) = H_2O + 0.5O_2 + 3.76N_2$.

The reaction transfers energy by heat

$Q = (10 \text{ moles})(h_{H2O}(1000K) + 0.5h_{O2}(1000K) + 3.76h_{N2}(1000K) - h_{H2}(500K) - h_{O2}(500K) - 3.76h_{N2}(500K))$

Given the elevated temperatures of the reactants and products, we model each species of molecules as an ideal gas. According to Table A.9,

$h_{H2O}(1000K) = (-241826 + 26000)$ J/mol
$h_{O2}(1000K) = 22703$ J/mol
$h_{N2}(1000K) = 21463$ J/mol

$h_{H2}(500K) = 5883$ J/mol
$h_{O2}(500K) = 6086$ J/mol
$h_{N2}(500K) = 5911$ J/mol

Inserting these values into the expression for Q, we obtain that

$Q = - 1579680$ J.

The negative sign indicates that this reaction transfers energy by heat from the reactor to the surroundings.

Adiabatic flame temperature

Consider a steady-state reaction. The body of the reactor is thermally insulated. Each stream of reactants enters the reactor at a known thermodynamic state. The products exit the reactor in a single stream of temperature T, called the *adiabatic flame temperature*.

The thermal insulation prevents energy transfer by heat between the reactor and surroundings, Q = 0. The conservation of energy requires that

$H_{products} = H_{reactants}$.

The enthalpy of reactants is determined by summing the enthalpies of all streams of reactants. Assume that the products form an ideal gas mixture, so that the enthalpy of products is a function of temperature only, and is determined by summing the enthalpies of individual products. The conservation of energy, $H_{products} (T) = H_{reactants}$, solves the absolute flame temperature.

Example. H_2 and 400% theoretical air enter a steady-state, adiabatic reactor at 25 Celsius. Determine the temperature of the products.

The equation of reaction is

$H_2 + 4x0.5(O_2 + 3.76\ N_2) = H_2O + 1.5O_2 + 7.52N_2$.

The reactants enter in the reference state, 25 Celsius, so that $H_{reactants} = 0$, and the temperature of the products is determined by solving the equation of $H_{products}\ (T) = 0$.

For 1 mole of H_2 entering the reactor, the enthalpy of products is

$H_{products}\ (T) = h_{H2O}(T) + 1.5h_{O2}(T) + 7.52h_{N2}(T)$.

The enthalpy of each species of molecules as a function of temperature is listed in Table A.9.

The equation $H_{products}\ (T) = 0$ is nonlinear, but we will find an approximate adiabatic flame temperature by linear interpolation.

At T = 1000 K, Table A.9 lists

$h_{H2O}(1000K) = (-241826 + 26000)$ J/mol
$h_{O2}(1000K) = 22703$ J/mol
$h_{N2}(1000K) = 21463$ J/mol

so that $H_{products}\ (1000K) = -20369$ J/mol.

At T = 1100 K, Table A.9 lists

$h_{H2O}(1100K) = (-241826 + 30190)$ J/mol
$h_{O2}(1100K) = 26212$ J/mol
$h_{N2}(1100K) = 24760$ J/mol

so that $H_{products}\ (1100K) = +\ 13877$ J/mol.

Because $H_{products}\ (1000K) < 0$ and $H_{products}\ (1100K) > 0$, the adiabatic flame temperature must falls between 1000 K and 1100 K. By linear interpolation,

$(T - 1000\ K)/(H_{products}\ (T) - H_{products}\ (1000K)) = (1100\ K - 1000\ K)/(H_{products}\ (1100K) - H_{products}\ (1000K))$.

Set $H_{products}\ (T) = 0$ in the above equation, and we obtain that

T = 1059 K.

This is an approximate adiabatic flame temperature.

Chemical equilibrium

Once again consider the reaction

$H_2 + 0.5O_2 = H_2O$.

Hydrogen and oxygen form water. Water split into hydrogen and oxygen. In equilibrium, the reactor will have all three species of molecules.

Degree of reaction

Denote the *degree of reaction* by ε. For the reaction $H_2 + 0.5O_2 = H_2O$, the degree of reaction ε is the number of hydrogen molecules consumed. When the reaction advances by dε, the amounts of the three species of molecules change by

$dn_{H2} = - d\varepsilon$,
$dn_{O2} = - 0.5d\varepsilon$,
$dn_{H2O} = + d\varepsilon$.

The negative sign means that the reaction reduces the amount of each reactant, and the positive sign means the reaction increases the amount of the product. Each stoichiometric coefficient proportions the change of the amount of a species of molecules.

Condition of chemical equilibrium

We assume that the reaction takes place in a cylinder sealed with a piston, so that no matter leaks in or out. The cylinder is in contact with a thermal reservoir of a fixed temperature T. A weight is placed above the piston, so that the piston can slide up and down, but the pressure in the cylinder is fixed at P.

We run BAT on the reaction. We identify an isolated system with internal variables. The isolated system has multiple parts: the mixture of molecules, the thermal reservoir, and the weight. The internal variables of the isolated system include the transfer energy by heat to the thermal reservoir, the change of height of the weight, and the degree of reaction.

Running the basic algorithm of thermodynamics, we identify a shadow of entropy, the Gibbs function. Let the Gibbs function of the mixture be $G(T, P, n_{H2}, n_{O2}, n_{H2O})$. Recall that

$dG = - SdT + VdP + \mu_{H2}dn_{H2} + \mu_{O2}dn_{O2} + \mu_{H2O}dn_{H2O}$.

When the reaction advances by dε under constant temperature and constant pressure, the Gibbs function changes by

$dG = (- \mu_{H2} - 0.5\mu_{O2} + \mu_{H2O})d\varepsilon$.

The change in the Gibbs function is expressed in terms of the chemical potentials of the three species of molecules in the mixture.

Under constant temperature and constant pressure, the BAT requires that the reaction move in the direction that reduces the Gibbs function. In chemical equilibrium, dG = 0 for any small changes dε. Consequently, the reaction reaches equilibrium when

$\mu_{H2} + 0.5\mu_{O2} = \mu_{H2O}$.

This condition of equilibrium is applicable in general, and is not limited to ideal gases. For example, H_2O molecules can be in any phase or any mixture of phases.

Exercise. Run the basic algorithm of thermodynamics on the reaction and find the shadow of entropy.

Ideal gas reaction

The merit of being ideal. A mixture of three species of molecules has two independent mole fractions:

$y_1 = n_1/(n_1 + n_2 + n_3)$,
$y_2 = n_2/(n_1 + n_2 + n_3)$.

The chemical potential for each species in the mixture is a function of temperature, pressure, and mole fractions, $\mu_1(T,P,y_1,y_2)$, $\mu_2(T,P,y_1,y_2)$, and $\mu_3(T,P,y_1,y_2)$. This information is rarely available when the mixture is not an ideal gas mixture. Consequently, the condition of equilibrium is hard to apply in general.

By contrast, the chemical potential of each species of molecules in an ideal gas mixture takes the form

$\mu_1(T,P,y_1,y_2) = \mu_1(T,P_0) + RT \log(y_1P/P_0)$.

Here R is the universal gas constant, P_0 is the reference pressure. The dependence on pressure and mole fraction takes a simple form. The reference chemical potential, $\mu_1(T,P_0) =$

$h_1(T) - Ts_1(T,P_0)$, is a function of a single variable, temperature. Both functions, $h_1(T)$ and $s_1(T,P_0)$, are listed in the ideal gas tables for each species of commonly used molecules.

Equilibrium constant. Consider a reaction in an ideal gas. For example, at a high temperature and low pressure, H_2O molecules form an ideal gas. Thus, all species of molecules in the reaction $H_2 + 0.5O_2 = H_2O$ are ideal gases.

The chemical potentials of the three species molecules in the mixture are

$$\mu_{H2}(T,P_{H2}) = \mu_{H2}(T,P_0) + RT \log(y_{H2}P/P_0),$$
$$\mu_{O2}(T,P_{O2}) = \mu_{O2}(T,P_0) + RT \log(y_{O2}P/P_0),$$
$$\mu_{H2O}(T,P_{H2O}) = \mu_{H2O}(T,P_0) + RT \log(y_{H2O}P/P_0).$$

Insert these chemical potentials into the condition of equilibrium, $\mu_{H2} + 0.5\mu_{O2} = \mu_{H2O}$, and write

$$(y_{H2O}{}^{1})/(y_{H2O}{}^{1}y_{O2}{}^{0.5})(P/P_0)^{1-1-0.5} = K,$$

where

$$RT \log K = \mu_{H2}(T,P_0) - 0.5\mu_{O2}(T,P_0) - \mu_{H2O}(T,P_0).$$

The dimensionless number K is called the *equilibrium constant*. This name is not quite right: The dimensionless number is not a constant, but is a function of temperature, K(T).

The condition of equilibrium shows the following trends.

- When K << 1, the reactants dominate the mixture in equilibrium. When K >> 1, the product dominates the mixture in equilibrium. When K is on the order of unity, comparable amounts of reactant and product constitute the mixture in equilibrium.
- K is a function of T. At room temperature, water dominates the mixture in equilibrium. As the temperature increases, the proportion of hydrogen and oxygen increases in the mixture in equilibrium.
- The power of pressure is the change in the number of molecules, counted using the stoichiometric coefficients: 1 - 1 - 0.5 = - 0.5. The reaction reduces the number of molecules, so that an increase in pressure increases the number of water molecules.

Equilibrium composition. The equilibrium composition depends on temperature and pressure. Let us find this dependence. Let $n^0{}_{H2}$, $n^0{}_{O2}$, and $n^0{}_{H2O}$ be the amounts of the three species of molecules in the cylinder before the reaction begins. When the reaction advances to a degree of reaction, ε, the amounts of the three species of molecules become

$$n_{H2} = n^0{}_{H2} - \varepsilon,$$
$$n_{O2} = n^0{}_{O2} - 0.5\varepsilon,$$
$$n_{H2O} = n^0{}_{H2O} + \varepsilon.$$

Inserting the above equations into the condition of equilibrium, we obtain a nonlinear algebraic equation for ε. The equation can be plotted as a function P(ε,T). Given T and P, this function determines the degree of reaction in equilibrium, ε, as well as the equilibrium composition, y_{H2}, y_{O2}, and y_{H2O}.

Exercise. Use chemical potentials to calculate the equilibrium constant for the reaction $H_2 + 0.5O_2 = H_2O$ at 1000 K.

Exercise. Derive the condition of equilibrium for an ideal gas reaction, $H_2 + 0.5O_2 = H_2O$, in a reactor of a constant volume.

Simultaneous reactions

A piston-cylinder reactor is held at a constant pressure P and a constant temperature T. In the cylinder are two simultaneous reactions:

$H_2 + 0.5O_2 = H_2O$,
$H_2 + 2OH = 2H_2O$.

Chemical reactions conserve every species of atoms. Let ε_1 be the degree of one reaction, and ε_2 be the degree of the other reaction. The conservation of every species of atoms requires that

$dn_{H2} = - d\varepsilon_1 - d\varepsilon_2$,
$dn_{O2} = - 0.5d\varepsilon_1$,
$dn_{OH} = - 2d\varepsilon_2$,
$dn_{H2O} = + d\varepsilon_1 + 2d\varepsilon_2$.

The degrees of the two reactions, ε_1 and ε_2, are independent internal variables.

Equilibrium at constant temperature and pressure minimizes the Gibbs function. Let the Gibbs function of the mixture be $G(T, P, n_{H2}, n_{O2}, n_{OH}, n_{H2O})$. Recall that

$$dG = - SdT + VdP + \mu_{H2}dn_{H2} + \mu_{O2}dn_{O2} + \mu_{OH}dn_{OH} + \mu_{H2O}dn_{H2O}.$$

At constant temperature and constant pressure, as the two reactions advance, the Gibbs function changes by

$$\begin{aligned} dG &= \mu_{H2}(- d\varepsilon_1 - d\varepsilon_2) + \mu_{O2}(- 0.5d\varepsilon_1) + \mu_{OH}(- 2d\varepsilon_2) + \mu_{H2O}(+ d\varepsilon_1 + 2d\varepsilon_2) \\ &= (- \mu_{H2} - 0.5\mu_{O2} + \mu_{H2O})d\varepsilon_1 + (- \mu_{H2} - 2\mu_{OH} + 2\mu_{H2O})d\varepsilon_2. \end{aligned}$$

The reactions equilibrate when the Gibbs function minimizes, so that

$\mu_{H2} + 0.5\mu_{O2} = \mu_{H2O}$,
$\mu_{H2} + 2\mu_{OH} = 2\mu_{H2O}$.

The conditions of equilibrium of simultaneous reactions consist of the condition of equilibrium of each individual reaction.

The two conditions of equilibrium lead to coupled nonlinear algebraic equations for the two degrees of reaction in equilibrium. Solving these equations, we determine the equilibrium composition.

Dimensionless chemical potential

This section is not required for applying thermodynamics. The section critiques Gibbs's definition of chemical potentials.

Flexibility in defining chemical potentials

So far we have adopted the following definition for chemical potential:

$\mu_1 = -T^{-1}\partial S(U,V,N_1,N_2)/\partial N_1$.

This definition is equivalent to that introduced by Gibbs (1875):

$\mu_1 = \partial U(S,V,N_1,N_2)/\partial N_1$.

We have already mentioned the flexibility in defining temperature. All that matters is the derivative $\partial S(U,V,N_1,N_2)/\partial U$. Any monotonically decreasing function of the derivative defines a temperature. Thermodynamics works just the same even if we do not give any name to this derivative. This enormous flexibility comes about because temperature has no definition outside thermodynamics. The choice adopted in thermodynamics, $1/T = \partial S(U,V,N_1,N_2)/\partial U$, is a historical accident.

We do not have any flexibility in defining pressure. We insist that the pressure in thermodynamics should recover the pressure in mechanics, force/area. We find that $P/T = \partial S(U,V,N_1,N_2)/\partial V$.

In defining chemical potentials, once again we have enormous flexibility, because chemical potentials have no definition outside thermodynamics.

What really matters is that the partial derivatives $\partial S(U,V,N_1,N_2)/\partial U$, $\partial S(U,V,N_1,N_2)/\partial V$, $\partial S(U,V,N_1,N_2)/\partial N_1$, and $\partial S(U,V,N_1,N_2)/\partial N_2$ play analogous roles. All these partial derivatives are equally significant because thermodynamics is a play of maximizing entropy. Even if we choose not to call these derivatives by any name, we will still be doing the same experiment and the same calculation. Naming the partial derivatives gives us verbal convenience. It is convenient to give each child a distinct name.

The particular definition of chemical potentials adopted in thermodynamics comes from Gibbs (1875), and is just a name given to a partial derivative. We do not need any reason to give a child a particular name. For this definition of chemical potential, we will find a reason for the presence of the negative sign, but we cannot find any reason for the presence of temperature.

Note that $\partial S(U,V,N_1,N_2)/\partial N_1$ is a dimensionless number, which means the increase of the logarithm of the number of quantum states associated with adding one molecule of species 1, while keeping the energy, volume, and number of molecules of species 2 fixed. The quantity $\partial S(U,V,N_1,N_2)/\partial N_1$ has clear significance. Gibbs twisted this number into a quantity to have the unit of energy/amount. He was perhaps too enamored with the supporting actor, energy. His reason was twisted, but his definition has stuck.

Exercise. Confirm that the above two definitions of chemical potential are equivalent.

Dimensionless chemical potential

Let $S(U,V,N_1,N_2)$ be the function that characterizes an open system capable of transferring molecular species 1 and 2. Define the dimensionless chemical potential of species 1 in the open system by

$\lambda_1 = -\partial S(U,V,N_1,N_2)/\partial N_1$.

Recall the definition of entropy, $S = \log \Omega$. By definition, entropy is absolute and dimensionless. The chemical potential is a dimensionless number, which measures the change in the number of quantum states associated with adding one molecule to the open system. Let us develop intuition for the dimensionless chemical potential by looking at simple systems.

Pure substance

Characterize a pure substance by T, P, s, u, v, h. All extensive properties are per molecule basis, and temperature is measured in the unit of energy. Characterize an open system of a pure substance by the function $S(U,V,N)$. By the definition of temperature, pressure, chemical potential, write

$dS = T^{-1}dU + (P/T)dV - \lambda dN$.

When the system increases the number of molecules by dN, but keeps the temperature and pressure fixed, dS = sdN, dU = udN, and dV = vdN. Inserting these expressions into the above equation, we obtain that

$\lambda = h/T - s$.

For a pure substance, the dimensionless chemical potential coincides with the negative Planck function per molecule.

Example. At 25 Celsius, 100 kPa, the absolute entropy of H_2O (liquid) is s = 69.960 J/mol-K. Remove the fake unit of entropy:

s = (69.960 J/mol-K)/(8.314 J/mol-K) = 8.414.

This is the dimensionless entropy per molecule.

At 25 Celsius, 100 kPa, the enthalpies of H_2 and O_2 are set to zero, and the enthalpy of H_2O (liquid) is h = -285830 J/mol. The enthalpy per molecule is

$h = -(285830 \text{ J/mol})/(6.022 \times 10^{23}/\text{mol}) = - 47464.30 \times 10^{-23}$ J

A “natural unit” for covalent energy is 1 eV = $1.6 \times 10^{--19}$ J. In this unit, h = - 2.97 eV.

Recall that 25 Celcius = 298.15 K = (298.15 K)(1.38×10^{-23} J/K) = 411.45×10^{-23} J. The dimensionless chemical potential is

$\lambda = - 115.359 - 8.414$.

The first term comes from enthalpy, and the second term comes from entropy.

Exercise. Update enthalpy and entropy in the steam tables for water, steam, and ice in three-phase equilibrium. Determine the dimensionless chemical potentials of H_2O in the three states.

Exercise. Update enthalpy and entropy in the steam tables for water and steam in equilibrium at 50 Celsius. Determine the dimensionless chemical potentials of H_2O in the two states.

Ideal gas

For an ideal gas, enthalpy is a function of temperature only, h(T), and the dimensionless entropy per molecule takes the form

$s(T,P) = s(T, P_0) - \log(P/P_0)$.

The result is uncluttered by the factor of unit conversion, the universal gas constant R. The dimensionless chemical potential is

$\lambda = h(T)/T - s(T, P_0) + \log(P/P_0)$.

Example. At 1000 K, 100 kPa, Table A. 9 lists for H_2 an enthalpy of 20663 J/mol and an entropy of 166.225 J/mol-K. Determine the dimensionless chemical potential.

In this example, P_0 = 100 kPa. The enthalpy per molecule is

$h = (20663 \text{ J/mol})/(6.022 \times 10^{23}/\text{mol}) = 3431.25 \times 10^{-23}$ J.

The dimensionless entropy per molecule is

$s = (166.225 \text{ J/mol-K})/(8.314 \text{ J/mol-K}) = 19.99$.

The dimensionless chemical potential is

$\lambda = 8.34 - 19.99$.

The first term comes from enthalpy, and the second term comes from entropy.

Summary of this play of thermodynamics

We have reached the end of this play of thermodynamics. Your curiosity and your determination to master the subject have been an inspiration to me. I thank you for the privilege of your time.

Our accomplishments

We have studied four types of systems:
- Isolated system
- Thermal system
- Closed system
- Open system

We have studied four material models:
- Pure substance
- Incompressible pure substance
- Ideal gas
- Ideal gas mixture

We have run the basic algorithm of thermodynamics (BAT) on an enormous number of applications:

- Dissipation of energy
- Degradation of energy
- Dispersion of ink
- Change of phases
- Osmosis
- Steady-flow devices (e.g., turbine, compressor, throttle, heat exchanger, nozzle, and diffuser)
- Cycles
- Power plants
- Refrigerators
- Internal combustion engines
- Psychrometrics
- The ascent of sap
- Chemical reactions
- Fuel cell

Isolated system

- An *isolated system* is a part of the world that does not interact with the rest of the world.
- An isolated system flips—rapidly and ceaselessly—among a set of *quantum states*, called the *sample space* of the isolated system.
- A system isolated for a long time flips to every one of its quantum states with equal probability.

- Denote the *number of quantum states* of an isolated system by Ω.
- Define the *entropy* of an isolated system by $S = k_B \log \Omega$.
- We will soon define temperature, and let the Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J/K be the conversion factor between two units of temperature, Joule and Kelvin. Thus, J/K is a fake unit, analogous to inch/cm.
- Entropy is dimensionless, extensive, absolute, thermodynamic property.

- Denote a set by X, such as a set of volumes, a set of energies, and a set of numbers of H_2O molecules.
- An *internal variable* (or a random variable) is a function that maps the sample space of an isolated system to a set X.
- When the internal variable is fixed at a value x in X, the isolated system flips among quantum states in a *subset of the sample space*.
- Denote the *number of quantum states* in the subset by Ω(x).
- Define the *subset entropy* by $S(x) = k_B \log \Omega(x)$.

- After the system is isolated for a long time, and after the internal variable is fixed at a value x for a long time, the system flips to every quantum state in the subset with equal probability, and is said to reach *equilibrium*.
- The subset is called a *thermodynamic state* specified by the value x.
- The internal variable x is called a *thermodynamic property*.
- When the internal variable x changes, the isolated system is said to undergo a *process*.

- The *basic algorithm of thermodynamics* (BAT) constitutes four steps:
- Step 1. Construct an isolated system with an internal variable x.
- Step 2. Find the subset entropy S(x).
- Step 3. A *reversible process* changes the internal variable x such that the subset entropy remains constant.
- Step 4. An *irreversible process* changes the internal variable x such that the subset entropy increases.

- In practice, we often identify an isolated system with multiple internal variables, each being a function that maps the sample space to a distinct set.

- An isolated system conserves energy, space, matter, and charge.
- Energy, space, matter, charge serve as internal variables.

Thermal system

- A *thermal system* exchanges energy with the rest of the world, but nothing else.
- A thermal system is a family of isolated systems characterized by a function S(U).

- *Temperature*, 1/T = dS(U)/dU.
- $dS = T^{-1}dU$.
- *Thermal capacity*, C = dU(T)/dT.

- *Helmholtz function*, F = U - TS.
- The Helmholtz function is a function of temperature, F(T).
- dF = -SdT.

- A *thermal reservoir* is a thermal system of a fixed temperature T.
- When the internal energy of the thermal reservoir changes by Q, the entropy of the thermal reservoir changes by Q/T.

Closed system

- A *closed system* exchanges energy and volume with the rest of the world, but nothing else.
- A closed system is a family of isolated systems characterized by a function S(U, V).

- $1/T = \partial S(U,V)/\partial U$
- $P/T = \partial S(U,V)/\partial V$
- $dS = T^{-1}dU + (P/T)dV$
- *Enthalpy*, $H = U + PV$
- *Constant-volume thermal capacit*y, $C_V = \partial U(T,V)/\partial T$
- *Constant-pressure thermal capacity*, $C_P = \partial H(T,P)/\partial T$

- *Helmholtz function*, $F = U - TS$
- $dF = -SdT - PdV$
- *Gibbs function*, $G = U + PV - TS$
- $dG = -SdT + VdP$

- We can define many, many more properties.
- For example, $\partial T(H,P)/\partial P$ is called the Joule-Thomson coefficient, which characterizes a throttle.
- As another example, $V^{-1}\partial V(T,P)/\partial T$ is called the constant-pressure coefficient of thermal expansion.
- An enormous number of relations exist among properties.

- Work and heat depend on process, and are defined by
- $dW = PdV$
- $dQ = dU + PdV$

Open system

- An *open system* exchanges energy, volume, and matter with the rest of the world.
- An open system is a family of isolated systems characterized by a function $S(U, V, N_1, N_2)$. Here we just list the numbers of molecules of two species, 1 and 2.
- Define the chemical potential μ_1 of species 1 in the open system by $-\mu_1/T = \partial S(U,V, N_1, N_2)/\partial N_1$.
- Define the chemical potential μ_2 of species 1 in the open system by $-\mu_2/T = \partial S(U,V, N_1, N_2)/\partial N_2$.
- $dS = T^{-1}dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$.

- Define the Helmholtz function by $F = U - TS$.
- $dF = -SdT - PdV + \mu_1 dN_1 + \mu_2 dN_2$.

- Define the Gibbs function by $G = U + PV - TS$.
- $dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2$.

Pure substance

- A *pure substance* consists of molecules of a single species.
- A fixed amount of a pure substance is modeled as a closed system.
- A homogeneous state is called a *phase*.
- A pure substance can equilibrate in one phase, a mixture of two phases, or a mixture of three phases.

- In a mixture, temperatures of different phases are equal.
- Such a property are called an *intensive property*
- Temperature and pressure are *intensive properties*.

- In a mixture, entropies of different phases are additive.
- Such a property is called an *extensive property*.
- Extensive properties include S, U, V, H, F, G, C_V, C_P.
- The entropy per unit mass is called the specific entropy, and is denoted by s.
- Similarly define a specific property for any extensive property.

- When a state of liquid and a state of gas equilibrate, the state of liquid is called a *saturated liquid*, and the state of gas is called the *saturated gas*.
- In an equilibrated mixture of liquid and gas, denote the specific entropy of the saturated liquid by s_f, and the specific entropy of the saturated gas by s_g.
- The mass fraction of gas in the mixture is called the *quality*, denoted by x.
- In an equilibrated mixture of liquid and gas, the specific entropy obeys the rule of mixture, $s = (1 - x)s_f + xs_g$.

- Two phases in equilibrium satisfy the following conditions:
- $T_f = T_g$
- $P_f = P_g$
- $h_f - T_f s_f = h_g - T_g s_g$

- In the T-v plane, the states of saturated liquid form a curve, and the states of saturated gas form another curve.
- The saturated liquid curve and the saturated gas curve form a dome.
- The top of the dome is called the *critical state*.

- In the T-P plane, all mixtures of a state of saturated liquid and a state of saturated gas collapse to a single point.
- All such points form a curve, called the liquid-gas phase boundary.
- The liquid-gas phase boundary terminates at the critical state.
- The slope of the phase boundary satisfies the Clapeyron equation: $dP/dT = (s_g - s_f)/(v_g - v_f)$.

- The chemical potential of molecules in a pure substance is $\mu(T, P) = u + Pv - Ts$.
- $-s = \partial\mu(T, P)/\partial T$.
- $v = \partial\mu(T, P)/\partial P$.

- Properties of a pure substance are found in tables and apps.
- For the state of water in the water-ice-steam equilibrium, the absolute entropy is 3.519 kJ/kg-K, and the enthalpy is -15984.36 kJ/kg.
- Properties of pure H_2O are listed in steam tables (NIST PDF).
- Steam tables commonly set the entropy and enthalpy to be zero for water in water-ice-steam equilibrium, and list entropy and enthalpy at any other state of H_2O relative to this state of water.
- Update the steam tables by adding 3.519 kJ/kg-K to each entry of entropy, and adding -15984.36 kJ/kg to each entry of enthalpy.
- Use the updated values of enthalpy and entropy to calculate the chemical potentials of various states of pure H_2O, $\mu(T, P) = h - Ts$.
- These chemical potentials are used to analyze chemical reactions.

Incompressible pure substance

- Liquids and solids change volume negligibly, and are often modeled as thermal systems.
- $dS = T^{-1}dU$
- $C(T) = dU(T)/dT$
- Thermal capacities for liquids and solids can be found in tables.

- A thermal system of a pure substance melts at a fixed temperature T_m.
- Denote the energy of melting by $U_B - U_A$. A historical (and no longer appropriate) name for this quantity is latent heat.
- Denote the entropy of melting by $S_B - S_A$.
- $1/T_m = (S_B - S_A)/(U_B - U_A)$.

- $\mu(T, P) = \mu(T, P_0) + (P - P_0)v(T)$

- The specific thermal capacity is 2.06 kJ/kg-K for ice.
- The specific thermal capacity is 4.18 kJ/kg-K for water.
- The energy of phase change is 334 kJ/kg from ice to water.

Ideal gas

- A fixed amount of an ideal gas is modeled as a closed system.
- We are mostly interested in **6** properties: TVpush.
- Each state of the ideal gas is specified by **2** properties, say T and P.
- The other **4** properties, S, V, U, H, are functions of T and P, called the equations of state.

- We have described these functions in several sections.
- We now collect all four functions here.

- Ideal gas
- Ideal gas law, $PV = nRT$.
- This equation expresses V as a function of P and T.
- Universal gas constant, $R = 8.314$ J/mol-K.
- $m = nM$, where m is the mass of the gas, and M is the mass per mole.
- Specific gas constant, R/M.
- $M_{H2O} = 18$ g/mol.
- $M_{air} = 28.8$ g/mol.

- Thermal energy of ideal gas
- $dU = nc_V(T)dT$
- $U = nu(T)$
- $dH = nc_P(T)dT$
- $H = nh(T)$
- $c_P = c_V + R$
- $h(T) = u(T) + R$
- The function $c_P(T)$ and $h(T)$ for various molecules can be found in tables.

- Work and heat are not properties, but depend on process.
- $dW = PdV$
- $dQ = dU + PdV$

- Constant-volume process, $dV = 0$.
- $dW = 0$
- $dQ = dU = nc_V(T)dT$

- Constant-pressure process, $dP = 0$.
- $dW = PdV$, $W_{12} = P(V_2 - V_1)$
- $dQ = dH = nc_P(T)dT$

- Isothermal process, $dT = 0$.
- $dW = PdV = nRTV^{-1}dV$, $W_{12} = nRT \log(V_2/V_1)$
- $dQ = dU + PdV = dW$

- Adiabatic process, $dQ = 0$.
- Recall that $dQ = dU + PdV = nc_V(T)dT + nRTV^{-1}dV$
- $dQ = 0$ means that $nc_V(T)dT + nRTV^{-1}dV = 0$.
- Assume constant thermal capacity, we obtain that
- $TV^{k - 1}$ = constant, where $k = c_P/c_V$.
- PV^k = constant.

- Integrate $dW = PdV$ to obtain work.
- Because the gas is assumed to change state slowly, the adiabatic process is isentropic.

- Theory of ideal gas
- $dS = (nc_P(T)/T)dT - (nR/P)dP$
- $S(T, P) = ns(T, P_0) - nR \log (P/P_0)$
- The function $s(T, P_0)$ for various species of molecules can be found in ideal gas tables.

- The chemical potential of molecules in a pure ideal gas is $\mu(T, P) = \mu(T, P_0) + RT \log(P/P_0)$, where $\mu(T, P_0) = h(T) - Ts(T,P_0)$.
- The function $h(T)$ and $s(T, P_0)$ for various species of molecules can be found in ideal gas tables.

Ideal gas mixture

- Let n_1 be the number of moles of species 1, and n_2 be the number of moles of species 2.
- $PV = (n_1 + n_2)RT$. That is, the ideal gas law applies to the total number of molecules.
- $P_1 = n_1RT/V$ is the partial pressure of species 1.
- $P_2 = n_2RT/V$ is the partial pressure of species 2.
- $U(T) = n_1u_1(T) + n_2u_2(T)$.
- $H(T) = n_1h_1(T) + n_2h_2(T)$.
- $S(T,P) = n_1(s_1(T,P_0) - R\log(P_1/P_0)) + n_2(s_2(T,P_0) - R \log(P_2/P_0))$.

- The chemical potential of species 1 in an ideal gas mixture is $\mu_1(T, P_1) = \mu_1(T, P_0) + RT \log(P_1/P_0)$, where $\mu_1(T, P_0) = h_1(T) - Ts_1(T,P_0)$.
- The Gibbs function of two-species mixture is $G = n_1\mu_1 + n_2\mu_2$.

Applications of thermodynamics

We have seen a large number of applications of thermodynamics. Every application displays the same pattern:

Describe a phenomenon. Examples include the function of a throttle, the ascent of sap, the processes in a power plant, the molecules in a reaction, and the function of a fuel cell.

Run the BAT. (1) Identify an isolated system with internal variables. (2) Find the subset entropy of the isolated system as a function of the internal variables. (3) Keep the subset entropy constant for a reversible process, including equilibrium. (4) Increase the subset entropy for an irreversible process.

Use data. This course is limited to four material models: pure substances, incompressible pure substances, ideal gases, and ideal gas mixtures. Know your steam tables and ideal gas tables.

Give predictions. Examples include the second-law efficiency, reversible work, equilibrium condition, and entropy generation.