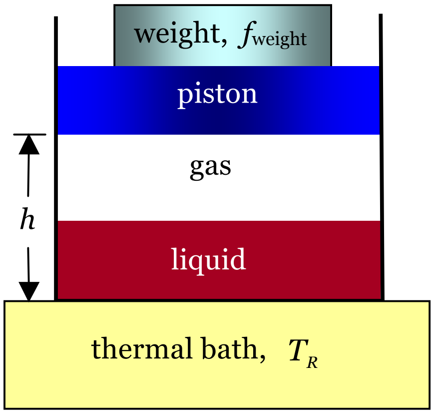
PRESSURE

We have developed a thermodynamic theory of (purely) thermal systems. A thermal system has a single independent variable: energy. The theory captures some experimental observations of solids and liquids. The theory, however, does poorly when compared to experimental observations involving gases. For example, the volume reduces drastically when a gas condenses into a liquid. We now develop a thermodynamic theory for systems with two independent variables: energy and volume.

A System with Variable Energy and Volume

A half bottle of wine. We regard a half bottle of wine as a system. The wine is a not a pure substance, and contains several species of molecules. The wine separates into two phases: liquid and gas. The two phases in the bottle together constitute "the wine".

We make the wine a *closed system*—that is, the wine and the rest of the world do not exchange matter, but exchange energy. We seal the bottle with a piston. The piston moves without friction, and does not let molecules leak. The wine is compressed by the weights, and is in thermal contact with a reservoir of energy (i.e., a thermal bath).



Model a closed system as a family of isolated systems. The half bottle of wine is a *closed system*—that is, a system that exchanges energy with the rest of the world, but not matter. We model the closed system as *a family of isolated systems*. Each member in the family is a system isolated for a long time, and is in a state of thermodynamic equilibrium. The family of isolated systems has two independent variables: internal energy U and volume V. The energy and the volume account for the contributions from both the liquid and the gas. When U and V are fixed to a pair of values for a long time, the wine is an isolated system in a state of thermodynamic equilibrium, flipping among a set of quantum states. When U and V are fixed to another pair of values for a long time, the wine is another isolated system in another state of thermodynamic equilibrium, flipping among another set of quantum states.

Going between two states of thermodynamic equilibrium. Between the two states of thermodynamic equilibrium, we temporary allow the wine to change the energy and volume by interacting with the rest of the world to change—that is, by moving the piston and by thermal contact with the reservoir of energy. Thus, one member in the family of isolated systems transform to another member by changing energy and volume. To qualify for the membership, each system must have been isolated for a long time and is in a state of thermodynamic equilibrium. During the *process* that transforms from one member to another, the piston moves and the thermal bath transfers energy. The process of transforming from one state of thermodynamic equilibrium to another, in general, brings the closed system—the wine—*out of equilibrium*. Gas bubbles move, and the wine near the thermal bath is hotter than other parts, etc. For the time being, we will focus on the states of thermodynamic equilibrium, and neglect the process of transformation.

Characterize the family of isolated systems by function $S(U,V)$. When the half bottle of wine is isolated at energy U and volume V for a long time, the isolated system flips among a set of quantum states with equal probability. Denote the number of quantum states is this set by $\Omega(U,V)$. The function $\Omega(U,V)$ characterizes the family of isolated systems. When we speak of having a thermodynamic model of a closed system, we mean that we know the function $\Omega(U,V)$. We will describe how this function may be determined experimentally, how this function is used to calculate other thermodynamic relations, and how this function is used to understand phenomena such as phase transition. But these will come later.

The logarithm of the number of quantum states is called the *entropy*. The entropy of the half bottle of wine isolated at energy U and volume V is $S(U,V)=\log\Omega(U,V)$. Consider two members in this family of isolated systems. One member is the wine isolated at (U,V), flips among a set of quantum states, and has the entropy $S(U,V)$. The other member is the wine isolated at $(U+dU,V+dV)$, flips among another set of quantum states, and has the entropy $S(U+dU,V+dV)$. The entropies of the two isolated systems differ by $dS=S(U+dU,V+dV)-S(U,V)$. According to calculus, given a function $S(U,V)$, when the energy changes by dU and the volume changes by dV, the entropy changes by

$$dS=\frac{\partial S(U,V)}{\partial U}dU+\frac{\partial S(U,V)}{\partial V}dV .$$

When we write dS, we always mean the difference in entropies of two states of thermodynamic equilibrium (U,V) and $(U+dU,V+dV)$. The process that transforms one state of thermodynamic equilibrium to the other can be non-equilibrium and interesting, but has nothing to do with the above equation.

Thermodynamic model of the reservoir of energy. A reservoir of thermal energy (or a thermal bath) is a system that maintains a fixed temperature T_R. The reservoir interacts with the rest of the world in only one manner: exchanging energy by heat. Thus, we model the reservoir as a family of isolated systems. Each member of this family has a distinct value of internal energy U_R and a distinct value of entropy S_R. The function $S_R(U_R)$ prescribes the thermodynamic model of the family of isolated systems.

Consider two members in this family of isolated systems. One member is the reservoir isolated at energy U_R, flips among a set of quantum states, and has the entropy $S_R(U_R)$. The other member is the reservoir isolated at energy $U_R + dU_R$, flips among another set of quantum states, and has the entropy $S_R(U_R + dU_R)$. The entropies of the two isolated systems differ by $dS_R = S_R(U_R + dU_R) - S_R(U_R)$. The lecture on temperature has related the changes in energy and entropy to temperature T_R:

$$dS_R = \frac{dU_R}{T_R}.$$

Because the temperature T_R is fixed, when the energy of the reservoir changes from U_{R1} to U_{R2}, the entropy of the reservoir changes by

$$S_{R2} - S_{R1} = \frac{U_{R2} - U_{S1}}{T_R}.$$

Thermodynamic model of the weight. The weight exerts on the piston a fixed force, f_{weight}. How is such a statement used in thermodynamics? We need to describe a thermodynamic model of the weight. The weight interacts with the rest of the world in only one manner: moving up and down. The weight has a fixed internal energy U_{weight} and a fixed entropy S_{weight}. That is, U_{weight} and S_{weight} are independent of the height of the weight, h. The potential energy of the weight is the force times the height, namely, $\text{potential energy of wieght} = f_{\text{weight}} h$. The sum of the potential energy of the weight and the internal energy of the weight gives the total energy E_{weight} of the weight: $E_{\text{weight}} = f_{\text{weight}} h + U_{\text{weight}}$.

The force due to the weight and the internal energy of the weight are both fixed parameters. When the height of the weight changes by δh, the total energy of the weight changes by

$$\delta E_{\text{weight}} = f_{\text{weight}} \delta h.$$

The quantity $-f_{\text{weight}} \delta h$ is called the *work* done by the weight.

Basic algorithm of thermodynamics. The lecture on entropy has formulated the basic algorithm:

1. Construct an isolated system with an internal variable, x.
2. When the internal variable is constrained at value x, the isolated system flips among a subset of its quantum states, and has entropy, $S(x)$.
3. Maximize the function $S(x)$ to determine the value of the internal variable x after the constraint is lifted for a long time.

Construct an isolated system with internal variables. The half bottle of wine, the reservoir of energy, and the weight together constitute a composite. We make the composite into an isolated system, and characterize it with many parameters. The isolated system has two *loading parameters*:

- the temperature of the reservoir, T_R,
- the force due to the weight, f_{weight}.

For the time being, we fix the values of the two loading parameters. The isolated system has several other *fixed parameters*:

- the area of the piston, A,
- the internal energy of the weight, U_{weight},
- the entropy of the weight, S_{weight}.

The isolated system has several *internal variables*:

- the energy of the wine, U,
- the volume of the wine, V,
- the height of the weight, h,
- the energy of the heat reservoir, U_R.

These internal variables are not all independent. They are constrained by the conservation of space and the conservation of energy.

Conservation of space. **Kinematics**. When the piston moves, the volume of the wine changes by dV and the height of the weight changes by dh. The changes of the two geometric parameters are related as

$$dV = Adh,$$

where A is the area of the piston. This relation is a consequence of the conservation of space: for the wine to gain volume, the weight has to move up. Geometric relations associated with movements of various parts of a system are also known as *kinematics*.

Conservation of energy. We have made the composite into an isolated system. According to the principle of the conservation of energy, the energy of the isolated system is constant, independent of the values of the internal variables, so that

$$dU + f_{\text{weight}} dh + dU_R = 0 .$$

The law of conservation of energy is also called the first law of thermodynamics: the change in the energy of wine, dU, equals the sum of the work done by the weight, $-f_{\text{weight}} dh$, and the heat received from the reservoir, $-dU_R$.

Entropy is additive. The conservation of space and the conservation of energy place two constraints among the variations of the four internal variables, dU, dV, dh, dU_R. Consequently, only two of the four are independent. We will take the energy and volume of the wine, *U* and *V*, to be the two independent internal variables. Thus, the composite—the wine, the weight and the reservoir together—is an isolated system with two independent internal variables: *U* and *V*.

The entropy of the composite, $S_{\text{composite}}$, is the sum of the entropies of the three parts: the wine, the weight and the heat reservoir, namely, $S_{\text{composite}} = S(U,V) + S_{\text{weight}} + S_R$. Using the constraints due to the conservation of space and the conservation of energy, we write the entropy of the composite as a function of *U* and *V*:

$$S_{\text{composite}} = S(U,V) - \frac{U}{T_R} - \frac{P_{\text{weight}} V}{T_R} .$$

We have dropped the additive constants. We have also substituted the force due to the weight by the pressure due to the weight, $P_{\text{weight}} = f_{\text{weight}} / A$.

Maximize the entropy of an isolated system as a function of internal variables. When *U* and *V* are fixed at particular values, the composite flips among a particular subset of quantum states. The entropy $S_{\text{composite}}(U,V)$ is the logarithm of the number of quantum states in this subset. The fundamental postulate requires that, when the wine, the weight and the heat reservoir equilibrate, the values of the internal variables (U,V) maximize the number of quantum states in the subset.

When the energy of the wine varies by dU and the volume of the wine varies by dV, the entropy of the composite varies by

$$dS_{\text{composite}} = \left[\frac{\partial S(U,V)}{\partial U} - \frac{1}{T_R} \right] dU + \left[\frac{\partial S(U,V)}{\partial V} - \frac{P_{\text{weight}}}{T_R} \right] dV .$$

Of all values of *U* and *V*, the most probable values maximize the function $S_{\text{composite}}(U,V)$. Thus, when the wine, the weight and the heat reservoir equilibrate, the number of quantum states becomes stationary—that is, $dS_{\text{composite}} = 0$ for arbitrary small variations dU and dV.

Because dU and dV are arbitrary and independent small variations, this condition of equilibrium requires that the quantity in front of each variation to vanish, leading to two separate equations:

$$\frac{1}{T_R} = \frac{\partial S(U,V)}{\partial U}, \qquad \frac{P_{\text{weight}}}{T_R} = \frac{\partial S(U,V)}{\partial V}.$$

The above equations apply when the wine, the weight and the reservoir equilibrate. The equations relate the loading parameters—the temperature of the reservoir and the force due to the weight—to the function characteristic of the half bottle of wine, $S(U,V)$.

The Gibbs equation. In the above, we have regarded T_R and P_{weight} as fixed loading parameters. The above two equations are still valid when we equilibrate the wine with another reservoir of a different temperature, and another weight with a different force. The two nonlinear algebraic equations determine the values of the energy and volume of the wine in equilibrium with the new reservoir and weight.

When the composite is in equilibrium, we can also speak of the temperature of the wine, T, and the pressure of the wine, P. We write

$$\frac{1}{T} = \frac{\partial S(U,V)}{\partial U}, \qquad \frac{P}{T} = \frac{\partial S(U,V)}{\partial V}.$$

The first equation recovers the definition of the temperature, and the second equation interprets the other partial derivative.

For a system of two independent variables (U,V), all other thermodynamic properties are functions of (U,V). Once we know the function $S(U,V)$, the partial derivatives of the function give the other two functions, $T(U,V)$ and $P(U,V)$. These functions constitute the *equations of state* of the wine.

For a given function $S = S(U,V)$, according to calculus, when the energy of the system varies by dU and the volume of the system varies by dV, the entropy of the system varies by

$$dS = \frac{\partial S(U,V)}{\partial U} dU + \frac{\partial S(U,V)}{\partial V} dV .$$

Comparing this equation to the two equations of state, we obtain that

$$dS = \frac{1}{T} dU + \frac{P}{T} dV .$$

This equation is due to Gibbs.

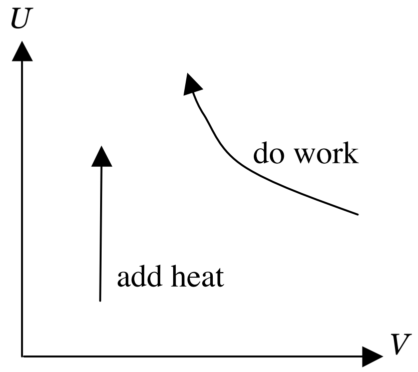
Experimental determination of $S(U,V)$. Given a system, we can experimentally measure U, V, P, T, and then integrate the above equation to obtain the function $S(U,V)$. We need be patient in such an experiment. Whenever you vary the loading parameters—the temperature of the heat reservoir and the force due to the weight—you must wait until the reservoir, the weight and the wine equilibrate.

We often choose an arbitrary thermodynamic state as a reference state, and measure the entropy at any other state relative to the reference state. We follow this practice with caution. Recall $S = \log \Omega$. Zero entropy is not something arbitrary, but has physical significance: it corresponds to an isolated system of a single quantum state.

Historically, the most prominent measurement of this kind has been to determine the function $S(U,V)$ for water. The experimental results are presented as tables, known as steam tables. Today, the function $S(U,V)$ is available online for many substances. For example, NIST maintains a website, http://webbook.nist.gov/chemistry/fluid/.

Graphic Representations

Represent a state of thermodynamic as a point in a plane. The volume V has absolute significance, but the energy U is significant up to an additive constant. A point in the plane represents a thermodynamic state of the system. A curve in the plane represents a sequence of states of thermodynamic equilibrium, known as a *quasi-equilibrium process*. For example, a vertical line represents adding energy to the system at a constant volume. That is, the piston remains fixed in position, the weight does no work, and the wine is in thermal contact with the heat reservoir.



As another example, we can thermally insulate the wine, but move the piston. This loading path is a curve in the (U,V) plane, known as an *adiabatic process*.

On the (U,V) plane, we can plot lines of constant entropy, constant temperature, and constant pressure. Such plots give graphical forms of the functions $S(U,V)$, $T(U,V)$, and $p(U,V)$.

Represent the function $S(U,V)$ as a surface in three dimensions. Following Gibbs, we represent the function $S(U,V)$ as a surface in the three-dimensional space, with (U,V) as the horizontal plane, and S as the vertical axis.

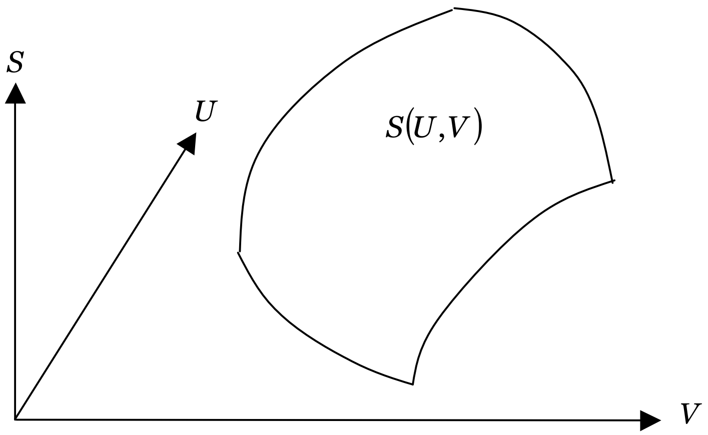
The volume V has absolute significance, but the energy U is significant up to an additive constant. We have set $S = 0$ for the ground state.

Recall the Gibbs equations:

$$\frac{1}{T} = \frac{\partial S(U,V)}{\partial U}, \qquad \frac{P}{T} = \frac{\partial S(U,V)}{\partial V}.$$

These two equations have clear graphical interpretations. Consider a plane tangent to the surface $S(U,V)$. The slope of the tangent plane with respect to the U axis is $1/T$, and the slope of the tangent plane with respect to the V axis is P/T.

While quantitative data are better represented by tables or contour lines on a plane, the three-dimensional representation is an extremely valuable tool to visualize the landscape of the function $S(U,V)$, and to provide theoretical insight into many salient experimental observations.



Graphical derivation of the conditions of equilibrium. We now use the three-dimensional representation to re-derive the conditions of equilibrium. For a system—such as a half bottle of wine—capable of two independent variations, U and V, the thermodynamics of the system is fully specified by the function $S(U,V)$. The wine is in contact with two loading devices: the weight of a fixed force f_{weight} and the heat reservoir of a fixed temperature T_R. The wine, the weight and the heat reservoirs together constitute an isolated system. The entropy of the composite is

$$S_{\text{composite}} = S(U,V) - \frac{U}{T_R} - \frac{p_{\text{weight}}V}{T_R}.$$

The isolated system has two internal variables U and V. According to the fundamental postulate, when the wine equilibrates with the weight and the heat reservoir, the values of U and V maximize the function $S_{\text{composite}}(U,V)$.

Following Gibbs (http://imechanica.org/node/654), we interpret the above statement geometrically. The function $S_{\text{composite}}(U,V)$ consists of two parts. One part is the entropy of the wine, which is the nonlinear function $S(U,V)$, represented in the three-dimensional space by the surface. The other part is the entropy of the heat reservoir, which is linear in U and V, represented in the three-dimensional space by an inclined plane passing through the origin of the space, with $1/T_R$ being the slope of the inclined plane with respect to the U axis, and p_{weight}/T_R being the slope of the inclined plane with respect to the V axis.

The vertical distance between the surface $S(U,V)$ and the inclined plane is the function $S_{\text{composite}}(U,V)$. Thermodynamics dictates that this vertical distance $S_{\text{composite}}(U,V)$ should maximize when the wine equilibrates with the weight and the heat reservoir.

For fixed loading parameters T_R and p_{weight}, the inclined plane is fixed. A plane parallel to the inclined plane may intersect with the surface $S(U,V)$ along a curve. All states along the curve give the equal value of the vertical distance $S_{\text{composite}}(U,V)$. The vertical distance between the two planes increases when we move upward the plane parallel to the inclined plane. From the geometry, the vertical distance $S_{\text{composite}}(U,V)$ is maximized when the plane parallel to the inclined plane becomes tangent to the surface $S(U,V)$. This geometric interpretation recovers the conditions of equilibrium:

$$\frac{1}{T_R}=\frac{\partial S(U,V)}{\partial U},\qquad \frac{p_{\text{weight}}}{T_R}=\frac{\partial S(U,V)}{\partial V}.$$

As stated before, at a point on the surface $S(U,V)$, we can form a plane tangent to the surface. The tangent plane has two slopes, in the directions of U and V. These slopes correspond to $1/T_R$ and p_{weight}/T_R.

When the loads, $1/T_R$ and p_{weight}/T_R, change gradually, the inclined plane rotates, and the associated tangent plane rolls along the surface $S(U,V)$ with two degrees of freedom.

State of equilibrium stable against large perturbation. Global maximization. If the surface $S(U,V)$ is convex, every tangent plane touches the surface at only one point, and only one state of equilibrium is associated with a pair of given loads $1/T_R$ and p_{weight}/T_R. By contrast, if part of the surface $S(U,V)$ is concave, a tangent plane may touch the surface at two points, and the two states of equilibrium are associated with a pair of given loads $1/T_R$ and p_{weight}/T_R.

For a partially concave surface $S(U,V)$, consider a tangent plane touching the surface at two points. Such a tangent plane can still be rolled and, while touching the surface at two points. But now the tangent plane can only be rolled with one degree of freedom. That is, when two states of equilibrium coexist, the two loading parameters $1/T_R$ and p_{weight}/T_R are related.

As the tangent plane touching the surface at two points rolls, the two points may merge to a single point. When the tangent plane is rolled beyond this special point, the tangent plane will touch the surface at only one point, and the tangent plane can be rolled with two degrees of freedom. This special point is known as the critical point.

It is possible for a tangent plane touches the surface at three points. This is the condition for the three states of equilibrium coexist. When the tangent plane touches the surface at three points, the tangent plane cannot be rolled further, so that the temperature and pressure for the three states to coexist are fixed.

Unless the surface is peculiar, no tangent plane can touch the surface at more than three points.

Theory of Phases

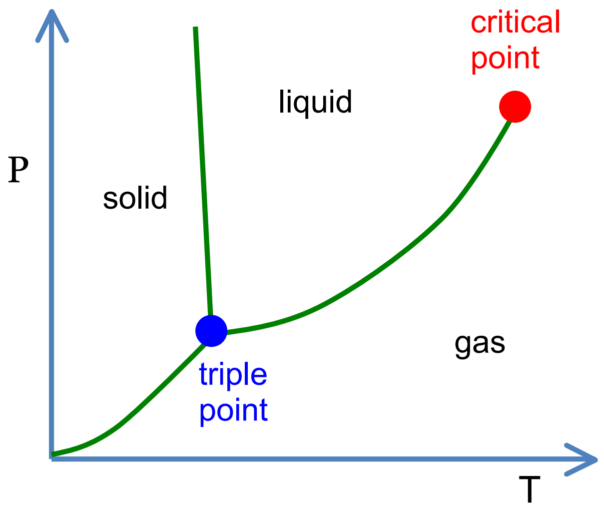
A pure substance as a closed system of two independent variables. We have studied a phase transition of a substance by using a model of a system with a single independent variable: energy. This single-variable model does reasonably well when compared with the experimental observation of a phase transition such as that from ice to water. The single-variable model, however, does poorly when compared to experimental observations of a transition from gas and liquid. A salient feature of this transition is that the volume reduces drastically when the gas condenses into a liquid. To accommodate this experimental observation and many others, we now model a pure substance as a closed system of two independent variables.

Phase diagram on the (*T*,*P*) plane. Many experimental observations are illustrated by a diagram on a (T,P) plane, known as a phase diagram of a pure substance. A point in the plane represents a given temperature and a given pressure. A region in the plane represents the range of temperature and pressure in which a phase is stable.

Between two neighboring regions is a curve, known as a *phase boundary*. When the temperature and the pressure fall on such a curve, two phases coexist.

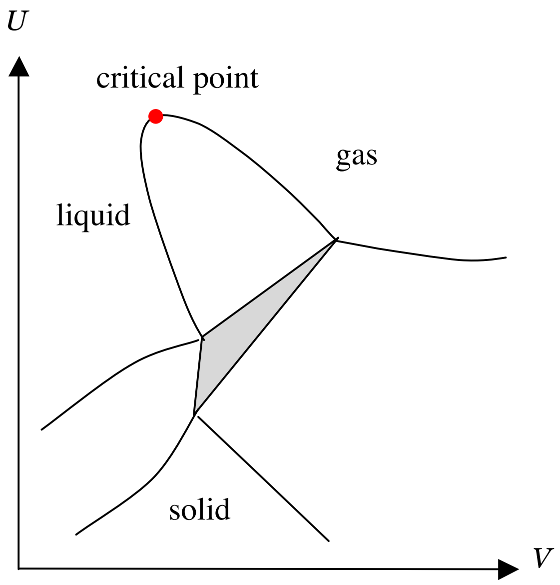
Three regions may share a common point, known as a *triple point*. When the temperature and pressure fall on precisely this point, three phases coexist.

The phase boundary between the gas and liquid terminates in the (T,P) plane at a point, known as the *critical point*.



Phase diagram on the (*U*,*V*) plane. Phase diagrams for many substances have been determined by experiments, and are available online. The salient features in the phase diagram can be understood within the two-variable model.

The phase diagram of a substance can also be drawn on planes of other coordinates. Here is a schematic phase diagram on the (U,V) plane. On this plane, each thermodynamic state of the substance is represented by a distinct point. For example, the states in which the three phases coexist are represented by the shaded triangle. When the three phases coexist, both energy and volume can still vary. By contrast, on the (T,P) plane, all the states in which the three phases coexist are represented by a single point.



Model a pure substance as a closed system of two independent variables. A pure substance aggregates a large number of molecules of a single species. The entropy S, energy U and volume V of a piece of the substance are proportional to the number of molecules in the piece, N. The entropy, energy and volume of the substance per molecule are

$$s = \frac{S}{N}, \qquad u = \frac{U}{N}, \qquad v = \frac{V}{N}.$$

The thermodynamics of the substance is fully specified by the function $s(u,v)$. This function is specific to the substance, and is independent of the size and shape of the piece. The temperature and pressure are given by

$$\frac{1}{T} = \frac{\partial s(u,v)}{\partial u}, \quad \frac{P}{T} = \frac{\partial s(u,v)}{\partial v}.$$

Analogous to the one-variable model (http://imechanica.org/node/291), for the two-variable theory, a single phase at a particular state (u,v) is stable against small perturbation if and only if the function $s(u,v)$ is a smooth and convex at the state (u,v). If the function $s(u,v)$ is nonconvex at the state (u,v), the entropy can be increased if the substance separates into different phases.

Coexistence of two phases. Next consider a mixture of two phases, A' and A''. We may regard the two phases as distinct systems, one characterized by a smooth and convex function $s'(u',v')$, and the other by a different smooth and convex function $s''(u'',v'')$. Let N' be the number of molecule in one phase, and N'' be the number of molecules in the other phase. When the two phases coexist, molecules can detach from one phase and attach to the other.

The total number of molecules in the mixture, N, is the sum of the numbers of molecules in the two phases:

$$N = N' + N''.$$

We neglect energy associated with the phase boundaries, so that the total energy of the mixture, U, is the sum of the energies of the two phases:

$$U = N'u' + N''u''.$$

Similarly, the total volume of the mixture, V, is the sum of the volumes of the two phases:

$$V = N'v' + N''v''.$$

Similarly, the entropy of the mixture, S, is the sum of the entropies of the two phases:

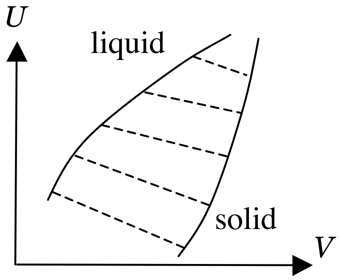
$$S = N's' + N''s''.$$

The above equations are known as the *rules of mixture*.

The rules of mixture have a simple graphical interpretation in the three-dimensional space of (S,U,V). Given a function $s'(u',v')$, the set of points (Ns',Nu',Nv') is a surface, representing the substance when all molecules are in phase A'. Similarly, given a function $s''(u'',v'')$, the set of points (Ns'',Nu'',Nv'') is a surface, representing the substance when all molecules are in phase A''.

Now pick one particular point on one surface, and pick another particular point on the other surface. According to the rules of mixture, the energy, the entropy and the volume of the mixture correspond to a point (S,U,V) on the straight line through the two points. The straight line connects the two states, and is called a *tie line*.

When N, U and V are fixed, the mixture is an isolated system with internal variables: N', N'', u', u'', v', v''. Of all values of the internal variables, the most probable ones maximize the entropy of the mixture. In the (S,U,V) space, when the energy and the volume of the mixture are fixed, the entropy of the mixture is maximized when the tie line is in a plane tangent to both surfaces. As the common tangent plane roll, the plane contacts the two surfaces at successive points.



A thermodynamic state of the mixture is represented by a point in the (U,V) plane. The set of tangent points on one surface projects to a curve in the (U,V) plane. The set of tangent points on another surface projects to another curve in the (U,V) plane. Also projected onto the (U,V) plane are the tie lines, the dashed lines in the figure.

From the graphical representation, we can directly read off the conditions for two phases to coexist. The two slopes of the tangent plane give the temperature and pressure. This interpretation recovers two facts: when the two phases equilibrate, both the temperature and the pressure are the same in the two phases:

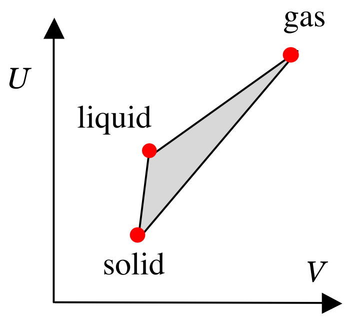
$$\frac{\partial s'(u',v')}{\partial u'} = \frac{\partial s''(u'',v'')}{\partial u''},$$
$$\frac{\partial s'(u',v')}{\partial v'} = \frac{\partial s''(u'',v'')}{\partial v''}.$$

For the two phases to coexist, the composite—the system and the heat reservoir together—should have the same entropy in the two phases, namely,

$$s'(u',v') - u'\frac{\partial s'(u',v')}{\partial u'} - v'\frac{\partial s'(u',v')}{\partial v'} = s''(u'',v'') - u''\frac{\partial s''(u'',v'')}{\partial u''} - v''\frac{\partial s''(u'',v'')}{\partial v''}.$$

Once the functions $s'(u',v')$ and $s''(u'',v'')$ are prescribed, the above are three nonlinear algebraic equations involving four unknowns: u', u'', v', v''. Consequently, for a substance of two independent variations, the mixture of two coexistent phases has one degree of freedom.

Coexistence of three phases. The three phases may be regarded as distinct systems, modeled by three functions: $s'(u',v')$, $s''(u'',v'')$, and $s'''(u''',v''')$. The three functions correspond to three surfaces in the (S,U,V) space. Pick one point from each surface. Through the three points draw a plane, known as the *tie plane*. A point in the tie plane represents a mixture of the three phases. When the energy and the volume are fixed for the mixture, the entropy of the mixture



maximizes when the tie plane are tangent to all three surfaces. The slope of this surface defines the pressure and temperature for the three phases to coexist, corresponding to the triple point in the phase diagram on the (p,T) plane. The tie plane is projected onto the (U,V) plane as the shaded triangle.

From the graphical representation, the conditions for the three phases to coexist are

$$\frac{\partial s'(u',v')}{\partial u'} = \frac{\partial s''(u'',v'')}{\partial u''} = \frac{\partial s'''(u''',v''')}{\partial u'''},$$

$$\frac{\partial s'(u',v')}{\partial v'} = \frac{\partial s''(u'',v'')}{\partial v''} = \frac{\partial s'''(u''',v''')}{\partial v'''},$$

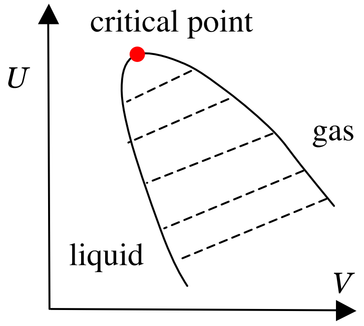
$$\begin{aligned}&s'(u',v') - u'\frac{\partial s'(u',v')}{\partial u'} - v'\frac{\partial s'(u',v')}{\partial v'}\\ &= s''(u'',v'') - u''\frac{\partial s''(u'',v'')}{\partial u''} - v''\frac{\partial s''(u'',v'')}{\partial v''}\\ &= s'''(u''',v''') - u'''\frac{\partial s'''(u''',v''')}{\partial u'''} - v'''\frac{\partial s'''(u''',v''')}{\partial v'''}\end{aligned}$$

Once the functions $s'(u',v')$, $s''(u'',v'')$ and $s'''(u''',v''')$ are prescribed, the above are six nonlinear algebraic equations involving six unknowns: u', u'', v', v'', u''',v'''. Consequently, for a substance of two independent variations, when three phases coexist, the mixture has no degree of freedom.

Many substances have more than three phases. For example, ice can be in several crystalline structures. Can four or more phases coexist? This is impossible for a system modeled with two independent variables. Each phase is modeled by a distinct function $s(u,v)$, corresponding to a surface in the three dimensional space (S,U,V). A plane can at most be tangent to three surfaces.

Critical point. Thomas Andrews (1869) reported the following experimental observation. At temperatures above 88 F, carbonic acid is a homogeneous fluid and undergoes no phase transition, even when a pressure of 400 atmospheres is applied.

Gibbs (1873) noted this experimental observation, and made the following theoretical interpretation. The liquid and the gas can be modeled by a single function $s(u,v)$, but the function is nonconvex. Consequently, when the energy and volume of the mixture are in a certain region, a plane can make be tangent to the surface $s(u,v)$ at two points. As the tangent plane rolls, the plane contacts the surface at two sets of



successive points, corresponding to two curves. The two curves merge at a point, and beyond this point the surface $s(u,v)$ is convex. This point is called the critical point.

Theory of Ideal Gases

Ideal gas. A flask of volume V contains N molecules. The molecules are called an ideal gas under the following conditions.

1. The kinetic energy of the molecules is so large that intermolecular interaction is negligible.
2. The distance between the molecules is so large that the probability of finding a molecule is independent of the location in the flask, and of the presence of other molecules.

Under such conditions, the total number of quantum states of the system is proportional to the total number of ways in which the N molecules can be distributed. The latter equals the product of the numbers of ways in which the individual molecules can be independently distributed. With N and U fixed, each of these numbers will be proportional to the volume of the flask V. The number of states is proportional to the Nth power of V, namely, $\Omega \propto V^N$. The proportional factor will depend on U and N, but not on V. Write

$$\Omega(U,V,N) = V^N \xi(U,N),$$

where $\xi(U,N)$ is a function of U and N. By definition, the entropy is $S = k_B \log \Omega$, so that

$$S = k_B N \log V + k_B \log \xi(U,N).$$

Inserting the above expression for entropy into the Gibbs equation involving the pressure,

$$\frac{P}{T} = \frac{\partial S(U,V,N)}{\partial V},$$

we obtain that

$$PV = Nk_B T.$$

This equation is the familiar law of ideal gases.

Inserting the expression for entropy into the other Gibbs equation,

$$\frac{1}{T} = \frac{\partial S(U,V,N)}{\partial U},$$

we obtain that

$$\frac{1}{T} = k_B \frac{\partial \log \xi(U,N)}{\partial U}.$$

This equation shows that the energy U is a function of temperature T and number N, and is independent of the volume V. The energy is extensive property, and is linear in the number of molecules N. Write

$$U = N\tilde{u}\left(T\right).$$

Here $\tilde{u}\left(T\right)$ is the internal energy per molecule. This function has been determined for many gases.

In summary, an ideal gas is governed by two equations of state: $PV = Nk_BT$ and $U = N\tilde{u}\left(T\right)$.

Entropic 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 bonds in the molecules, but from the fact that the number of quantum states increases with the volume. Such elasticity is known as *entropic elasticity*.

Expression for the function $S(U, V, N)$. As described above, an ideal gas satisfies

$$PV = k_BNT .$$

We now adopt the approximation that the heat capacity per molecule, $\tilde{c}_v$, is a constant for a given species of molecules. The energy of an ideal gas is given by

$$U = N\tilde{c}_vT .$$

Inserting the above relations into the Gibbs equation

$$dS = \frac{1}{T}dU + \frac{P}{T}dV ,$$

we obtain that

$$dS = \frac{dN}{U}dU + \frac{Nk_B}{V}dV .$$

Integrating, we obtain that

$$S\left(U,V,N\right) = S\left(U_0,V_0,N\right) + N\tilde{c}_v \log\left(\frac{U}{U_0}\right) + Nk_B \log\left(\frac{V}{V_0}\right),$$

where U_o and V_o are arbitrary reference values. The number of quantum states is

$$\Omega\left(U,V,N\right) = \Omega\left(U_0,V_0,N\right)\left(\frac{U}{U_0}\right)^{N\tilde{c}_v/k_B}\left(\frac{V}{V_0}\right)^N .$$

Per mole. The number of atoms in 12 grams of carbon is called a mole. (In this definition, each carbon atom used must be of the kind of isotope that has 6 neutrons.) Experimental measurements give

$$1 \text{ mole} \approx 6.022\times 10^{23}.$$

This number is called Avogadro's number N_A.

Let N be the number of molecules, and $n = N/N_A$ be the number of moles. The law of ideal gases becomes

$$PV = n\bar{R}T \ ,$$

where

$$\bar{R} = k_B N_A = 8.314\mathrm{J}/\left(\mathrm{K}\cdot\mathrm{mole}\right).$$

The constant $\bar{R}$ is known as the universal gas constant.

Per unit mass. Let m be the mass of a flask of a gas, let $v = V/m$ be the volume of gas per unit mass (i.e., the specific volume). The law of ideal gases can be written as

$$Pv = RT \ .$$

The constant R is different for each gas, given by

$$R = \frac{\bar{R}}{M},$$

where M is the mass per mole,

$$M = \frac{m}{n}.$$

For steam, H_2O, the mass per mole is $M = 18.015\mathrm{kg/kmol}$, and the gas constant is $R = 0.4615\mathrm{kJ}/\left(\mathrm{kg}\cdot\mathrm{K}\right)$.

Specific heat. For an ideal gas, the internal energy is a function of temperature, and is independent of the volume, $U = mu\left(T\right)$. Define the specific heat by

$$c_v = \frac{du\left(T\right)}{dT} \ .$$

The enthalpy is $h = u + Pv$. For an ideal gas, the entropy is also a function of temperature, $h = u\left(T\right) + RT$. Define another specific heat:

$$c_P = \frac{dh\left(T\right)}{dT} \ .$$

For an ideal gas, the specific heats of the two types are related by

$$c_P = c_v + R \ .$$

Entropy of ideal gas. Recall the Gibbs equation:

$$ds = \frac{1}{T}du + \frac{P}{T}dv \ .$$

Inserting into this equation the two equations of state of an ideal gas, $du = c_v(T)dT$ and $Pv = RT$, we obtain that

$$ds = \frac{c_v(T)}{T}dT + \frac{R}{v}dv .$$

We now adopt the approximation that the specific heat is a constant independent temperature. Integrating the above equation, we obtain that

$$s_2 - s_1 = c_v \log\left(\frac{T_2}{T_1}\right) + R\log\left(\frac{v_2}{v_1}\right).$$

An isentropic process keeps the entropy constant. The above expression shows that the isentropic process is given by

$$T^{c_v}v^R = \text{constant} .$$

Using the law of ideal gases $Pv = RT$, we can also express the condition for an isentropic process as

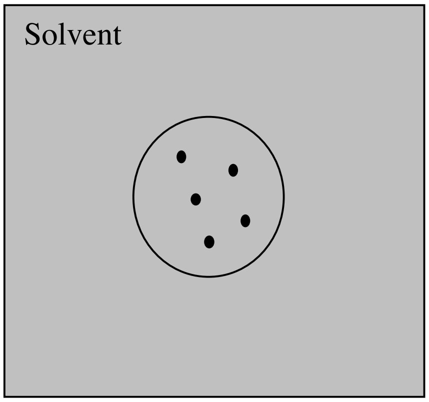
$$Pv^k = \text{constant} ,$$

where $k = c_p / c_v$.

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. When the particles are molecules, we call them solutes. When the particles are somewhat larger, say from 10 nm to 10 μm, we call them colloids. The bag is immersed in a reservoir of pure water. The bag is made of a *semi-permeable* membrane: water can permeate through the membrane but the particles cannot.

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 Gibbs equation involving pressure,

$$\frac{P}{T} = \frac{\partial S(U,V)}{\partial V} .$$

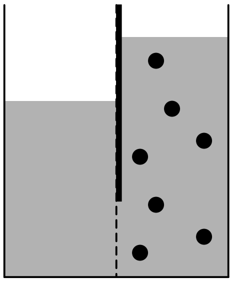
Inserting the expression $\Omega \propto V^N$, we obtain that

$$P = \frac{N}{V} k_B T \ .$$

This pressure is known as the *osmotic pressure*.

In equilibrium, 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 reservoir outside the bag. The difference in the concentration of particles in the bag and that of particles in the reservoir causes a difference in the pressures in the bag and in the reservoir. The difference in pressures can be balanced by the tension in the membrane.

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 the 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.



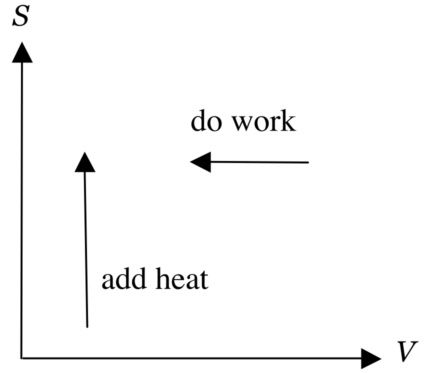
Breed Thermodynamic Properties

Entropy $S(U,V)$. We now return to the general problem of a system of variable energy and volume (i.e., a closed system). We model the closed system as a family of isolated systems. Each member in the family is a system isolated for a long time, flips among a set of quantum states with equal probability, i.e., is in a state of thermodynamic equilibrium. We transform one member to another by heat and work. We have focused on five thermodynamic properties: P, T, V, U, S. We specify all isolated systems in the family by two independent variables, U and V. The other three properties are functions of state—that is, we represent each property as a function of two independent variables: $S(U,V)$, $P(U,V)$, $T(U,V)$. We may wish to call these three functions of state equations of state.

In practice, we can obtain the function $S(U,V)$ by experimental measurement. The two other functions $P(U,V)$ and $T(U,V)$ are obtained the Gibbs equations:

$$\frac{1}{T} = \frac{\partial S(U,V)}{\partial U}, \qquad \frac{P}{T} = \frac{\partial S(U,V)}{\partial V}$$

We can also eliminate U from $P(U,V)$ and $T(U,V)$ to obtain $P(V,T)$. It turns out that we can use the function $S(U,V)$ to generate many more functions of state (i.e. thermodynamic properties). We next consider some common examples.



Energy $U(S,V)$. Consider a system (e.g., a half bottle of wine) characterized by a function $S(U,V)$. When the volume is fixed, the more energy the system has, the more quantum states the system has—that is, at any fixed V $S(U,V)$ is a monotonically increasing function of U. According to calculus, the function $S(U,V)$ can be inverted to obtain the function $U(S,V)$.

Of course, the two functions contain the same information of the same system: the half bottle of wine capable of two independent variations. The two functions are represented by the same surface in the three-dimensional space (S,U,V). There is no advantage in choosing one set of independent variables over another. Whatever preferences we might feel are all in our minds, and have nothing to do with the half bottle of wine.

We can represent the thermodynamic states of the system on the plane with coordinates S and V. A point in the plane represents a thermodynamic state, and a curve in the plane represents a loading path.

Thus, a thermodynamic state can be represented by a point on the (U,V) plane, or by a point on the (S,V) plane. The points in the two planes are mapped 1-to-1 by the function $S(U,V)$.

Now we put equations together. We characterize a system by a function $U(S,V)$. According to calculus, when the entropy varies by dS and the volume varies by dV, the energy varies by

$$dU = \frac{\partial U(S,V)}{\partial S} dS + \frac{\partial U(S,V)}{\partial V} dV .$$

Recall the Gibbs equation

$$dS = \frac{1}{T} dU + \frac{P}{T} dV .$$

Rearranging, we obtain that

$$dU = TdS - PdV .$$

This equation shows the two ways to change energy of the wine. The first term represents adding heat to the wine, and the second term represents doing work to the wine.

A comparison of the two expressions for dU gives that

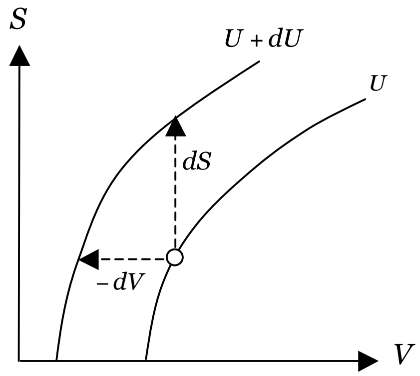
$$T = \frac{\partial U(S,V)}{\partial S}, \quad P = -\frac{\partial U(S,V)}{\partial V} .$$

The first equation recovers the definition of the temperature. The second equation is also familiar to many of us, probably because we have been told many times.

The system is capable of two independent variations, S and V. When S and V are specified, U is obtained from the function $U(S,V)$, whereas T and P are obtained from the partial derivatives.

In the three-dimensional space (S,U,V), a surface represents the function $U(S,V)$. A point on the surface represents a thermodynamic state. At the point and tangent to the surface we can form a plane. The two slopes of the tangent plane represent p and T.

We can also project the above interpretation to the (S,V) plane. On this plane all thermodynamic states of constant energy form a curve. We draw two such constant-energy curves, one for U and the other for $U + dU$. The gradient of the contour lines in one direction gives the temperature, and that in the other direction gives the pressure.



Legendre transform. A potent way to breed thermodynamic properties is Legendre transform. This mathematical dance is a topic in calculus, but is rarely taught in courses in calculus. You might wish to learn more about this piece of mathematics online. Here we focus on a few steps of immediate use to thermodynamics.

A Legendre transform turns a derivative of one function to an independent variable of a modified function. Given a function $z(x,y)$, denote the partial derivatives by

$$M = \frac{\partial z(x,y)}{\partial x}, \quad N = \frac{\partial z(x,y)}{\partial y}.$$

The increment in the function is given by

$$dz = Mdx + Ndy.$$

Define a new quantity

$$L = z - Mx.$$

A combination of the above two relations gives that

$$dL = -xdM + Ndy.$$

We now regard L as a function of M and y. According to calculus, the partal derivatives of the functions are

$$-x = \frac{\partial L(M,y)}{\partial M}, \quad N = \frac{\partial L(M,y)}{\partial y}.$$

The function $L(M,y)$ is called a Legendre transform of the function $z(x,y)$. A Legendre transform turns a derivative into an independent variable. We next use this piece of mathematics to breed thermodynamic properties.

Enthalpy $H(S,P)$**.** The wine and the weight together constitute a system with energy

$$H = U + PV .$$

The quantity H is known as the *enthalpy* of the wine. The terminology is clearly unfair to the weight.

Taking differential of $H = U + PV$, we obtain that

$$dH = dU + PdV + VdP .$$

Recall that $dU = TdS - PdV$. The above equation becomes that

$$dH = TdS + VdP .$$

When the pressure is fixed, dH is the heat added to the system. The coefficients in the above differential form are the partial derivatives:

$$T = \frac{\partial H(S,P)}{\partial S},\ V = \frac{\partial H(S,P)}{\partial P} .$$

Helmholtz function $F(T,V)$**.** The lecture on temperature has defined the Helmholtz function:

$$F = U - TS .$$

Taking differential of the function $F = U - TS$, we obtain that

$$dF = dU - TdS - SdT .$$

Recall that $dU = TdS - PdV$. The above equation becomes that

$$dF = -SdT - PdV .$$

We can regard F as a function of T and V. The coefficients in the above differential form are the partial derivatives of the function $F(T,V)$:

$$-S = \frac{\partial F(T,V)}{\partial T},\ -P = \frac{\partial F(T,V)}{\partial V} .$$

Gibbs function $G(T,P)$**.** Define the Gibbs function by

$$G = U - TS + PV .$$

Its differential form is

$$dG = -SdT + VdP .$$

The coefficients in the differential form are defined by the partial derivatives of the function $G(T,P)$.

$$-S = \frac{\partial G(T,P)}{\partial T},\ V = \frac{\partial G(T,P)}{\partial P} .$$

Properties defined by partial derivatives. Define the heat capacity under constant volume by

$$C_V = \frac{\partial U(T,V)}{\partial T}.$$

Define the heat capacity under constant pressure by

$$C_P = \frac{\partial H(T,P)}{\partial T}.$$

Other commonly used partial derivatives include the coefficient of thermal expansion,

$$\beta = \frac{\partial V(T,P)}{V\partial T},$$

isothermal compressibility,

$$\alpha = \frac{\partial V(T,P)}{V\partial P},$$

and the Joule-Thompson coefficient:

$$\mu = \frac{\partial T(P,H)}{\partial P}.$$

Maxwell relations. Given a function $z(x,y)$, calculus tells us that

$$\frac{\partial^2 z(x,y)}{\partial x \partial y} = \frac{\partial^2 z(x,y)}{\partial y \partial x}.$$

This identity in calculus is used in thermodynamics as follows. Write the increment of the function $z(x,y)$ as

$$dz = Mdx + Ndy.$$

The two coefficients are the partial derivative of the function

$$M = \frac{\partial z(x,y)}{\partial x}, \quad N = \frac{\partial z(x,y)}{\partial y}.$$

The mathematical identity of the second derivative now becomes that

$$\frac{\partial M(x,y)}{\partial y} = \frac{\partial N(x,y)}{\partial x}.$$

Such a relation can be applied to any function in thermodynamics, and is known as a Maxwell relation.

As an example, consider the Helmholtz function $F(T,V)$. Its increment is

$$dF = -SdT - PdV.$$

We can regard F as a function of T and V. The coefficients in the above differential form are the partial derivatives of the function $F(T,V)$:

$$-S = \frac{\partial F(T,V)}{\partial T}, \ -P = \frac{\partial F(T,V)}{\partial V}.$$

The associated Maxwell relation is

$$\frac{\partial S(T,V)}{\partial V} = \frac{\partial P(T,V)}{\partial T}.$$

Function $S(T,V)$. Following calculus, we write the increment of this function as

$$dS = \frac{\partial S(T,V)}{\partial T} dT + \frac{\partial S(T,V)}{\partial V} dV .$$

When volume is fixed, the closed system becomes a purely thermal system. Recall the Clausius-Gibbs relation for a purely thermal system:

$$dS = \frac{dU(T)}{T}.$$

By definition, this relation is applicable to a closed system when the volume is fixed. Write

$$\frac{\partial S(T,V)}{\partial T} = \frac{\partial U(T,V)}{T \partial T}.$$

Recall the definition of heat capacity:

$$\frac{\partial S(T,V)}{\partial T} = \frac{C_V(T,V)}{T}.$$

Use this identity to replace the first term in the expression of dS, and use the Maxwell relation to replace the second term. We obtain that

$$dS = \frac{C_V(T,V)}{T} dT + \frac{\partial P(T,V)}{\partial T} dV .$$

The above equation expresses the increment in entropy in terms comfortable to some people. Recall the Gibbs equation

$$dS = \frac{1}{T} dU + \frac{P}{T} dV .$$

This equation regards entropy as a function $S(U,V)$. There is no reason to feel that this equation is any less convenient.

Basic Algorithm of Thermodynamics in Terms of Free Energy

A system with variable energy and volume, as well as an internal variable. We return to general discussion to a system capable of two independent variations, the energy U and the volume V. In the case of the half bottle of wine, beside adding heat and doing work to the wine, we may be interested in an internal variable, for example, the number of molecules in the gas phase of the wine.

Entropy $S(U,V,Y)$. In generic terms, let Y be an internal variable of the system, and model the system by a function $S(U,V,Y)$. When U and V are fixed, but Y is allowed to take any value, the system is an isolated system with an internal variable. As dictated by the basic algorithm of thermodynamics, the internal variable Y changes to maximize the function $S(U,V,Y)$.

Internal energy $U(S,V,Y)$. For a system with an internal variable Y, we can invert the function $S(U,V,Y)$ to obtain $U(S,V,Y)$. The two functions characterize the same system. When S and V are fixed, the internal variable Y changes to minimize the function $U(S,V,Y)$.

Enthalpy $H(S,P,Y)$. Define the enthalpy by $H = U + PV$. When the pressure P is due to a fixed weight, the enthalpy is just the sum of the energy of the system and the weight. When (S,P) are fixed, the internal variable Y changes to minimize the function $H(S,P,Y)$.

Helmholtz function $F(T,V,Y)$. Define the Helmholtz function by $F = U - TS$. When (T,V) are fixed, the system is a thermal system in thermal equilibrium with a reservoir of energy. As shown in the lecture on temperature, the internal variable Y changes to minimize the function $F(T,V,Y)$.

Gibbs function $G(T,P,Y)$. Define the Gibbs function by $G = U - TS + PV$. When (T,P) are fixed, the system and the fixed weight together constitute a thermal system in thermal equilibrium with a reservoir of energy. The internal variable Y changes to minimize the function $G(T,P,Y)$.

Van der Waals equation. See slides.

Maxwell Construction. See slides.

Use (T,P) as independent variables. Because coexistent phases have the same temperature and the same pressure, we may wish to use (T,P) as the independent variables to represent the thermodynamic model, and organize experimental data. The phase diagram for CO_2 given above is an example. In the (T,P) plane, we can indicate individual phases, two-phase boundaries, triple point, and critical point. Within each the region of each phase, we can plot contours of experimentally measured energy, volume, and entropy.

Let $g'(T,P)$ and $g''(T,P)$ be the Gibbs functions per molecule of the two phases. The Gibbs function for the mixture is

$$G = N'g'(T,P) + N''g''(T,P).$$

The mixture is regarded as a system of fixed values of (T,P), and with an internal variable N'. Thermodynamics requires that G be minimized by varying N', while holding (T,p) fixed. We distinguish three situations:

- When $g'(T,P) < g''(T,P)$, all molecules should be in phase A'.
- When $g'(T,P) > g''(T,P)$, all molecules should be in phase A''.
- When $g'(T,P) = g''(T,P)$, the two phases coexist, namely, some of the molecules are in phase A', and other molecules are in phase A''.

Van der Waals equation, Maxwell Construction, Claypeyron equation. See slides.

Claypeyron equation. See slides. Along a two-phase boundary, show that

$$\frac{dP}{dT} = \frac{s''-s'}{v''-v'}.$$

This result is known as the Claypeyron equation.

Exercise. Find the data for entropies and volumes at the melting point of water. How much shift in the melting point is expected under 1 GPa of pressure? See slides.

Exercise. Derive an approximate relation between the vapor pressure as a function of temperature. Assume that for the same number of molecules, gas occupies much larger volume than liquid. The gas obeys the ideal gas law. The latent heat is insensitive to temperature. See slides.

Exercise. Derive an expression of the density of oxygen as a function of elevation from the surface of the earth.

Exercise. Use (T,V) as independent variables. Sketch function $F(T,V)$ on the plane (F,V) for several temperatures around the critical temperature. Sketch the corresponding curves on the (P,V) plane.

Exercise. Use (S,P) as independent variables. Sketch function $H(S,P)$ on the plane (H,S) for several pressures around the critical pressure. Sketch the corresponding curves on the (T,S) plane.

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