

## Pressure

So far we have been mainly concerned with a system of a single independent variable: energy (<http://imechanica.org/node/291>). The thermodynamics of such a system is fully specified by giving entropy as a function of energy,  $S(U)$ . The function stands for the logarithm of the number of quantum states of the system isolated at a particular value of energy, and can be determined by experimental measurement. Once the function  $S(U)$  is known, all other thermodynamic relations of the system can be calculated. The temperature  $T$  of the system is defined by  $1/T = dS(U)/dU$ , and the heat capacity  $C$  of the system is defined by  $1/C = dT(U)/dU$ . Both  $T$  and  $C$  are also functions of  $U$ .

We now consider a system of two independent variables: energy and volume. The thermodynamics of such a system is fully specified by giving entropy as a function of energy and volume,  $S(U, V)$ . The temperature  $T$  and the pressure  $p$  of the system are defined by  $1/T = \partial S(U, V)/\partial U$  and  $p/T = \partial S(U, V)/\partial V$ . These expressions lead to an experimental procedure to determine the function  $S(U, V)$  for a given system. Once the function  $S(U, V)$  is known, all other thermodynamic relations of the system can be calculated.

The laws of ideal gases and osmosis are derived. They illustrate entropic elasticity.

For a system in contact with a heat reservoir and subject to a force, the conditions of equilibrium can be represented graphically in the three dimensional space with  $S$ ,  $U$  and  $V$  as axes. This graphical representation is applied to a pure substance, leading to a theoretical understanding of salient experimental observations of coexistent phases.

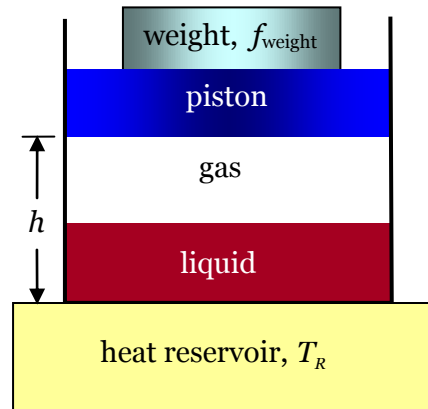
For any system characterized by variable energy and volume, the thermodynamic model of the system can also be represented by functions other than  $S(U, V)$ . Alternative representations include the energy  $U(S, V)$ , the enthalpy  $H(S, p)$ , the Helmholtz function  $F(V, T)$ , and the Gibbs function  $G(T, p)$ . These alternative representations add no physical content to the theory, but may provide mathematical convenience.

Several other mathematical ideas are described in Appendices, including the linearized equations of state, Hessian, Legendre transformation, and Maxwell relations.

**A system with variable energy and volume.** A half bottle of wine is a system. The system contains several species of molecules, and separates into

two phases, liquid and gas. Both phases in the half bottle of wine are included when we refer to “the wine”.

The wine interacts with the rest of the world in two modes. The bottle is sealed with a piston. We can fix the position of the piston, and *add heat* to the wine by bringing the wine into thermal contact with a heat reservoir. Alternatively, we can thermally insulate the wine, and *do work* to the wine by moving the piston down with a weight.



We can place the wine under weights of different forces, and in thermal contact with heat reservoirs of different temperatures. We can add heat and do work to the half bottle of wine in sequence and in combination. We can arrange the sequence to convert heat into work, or the other way around. That is, we can make the half bottle of wine into a thermomechanical transducer—an engine or a refrigerator.

We block all other modes of interaction. For example, the molecules of the wine do not escape from the bottle. A system is called a *closed system* if it can exchange energy with the rest of the world by receiving work and heat, but does not exchange matter with the rest of the world. In the example of the half bottle of wine, the work is done by the weight.

**Thermodynamic model of the wine.** We model the half bottle of wine as a system of two independent variables: 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, the wine becomes an isolated system, flipping among a set of quantum states. When  $U$  and  $V$  are fixed to another pair of values, the wine becomes another isolated system, flipping among another set of quantum states.

Let  $\Omega(U, V)$  be the number of quantum states of the half bottle of wine isolated at energy  $U$  and volume  $V$ . This function constitutes the thermodynamic model of the wine. When we speak of having a thermodynamic model of a 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.

We will keep calling the quantity  $S = \log \Omega$  the entropy. The entropy of the half bottle of wine isolated at energy  $U$  and volume  $V$  is a function

$$S = S(U, V).$$

According to calculus, when the energy of the wine varies by  $\delta U$  and the volume of the wine varies by  $\delta V$ , the entropy of the wine varies by

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

**Experimental determination of  $S(U, V)$ .** In the lecture on temperature (<http://imechanica.org/node/291>), one partial derivative has been related to the temperature  $T$ :

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

In this lecture, the other partial derivative will be related to the temperature  $T$  and pressure  $p$ :

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

Given a system, we can experimentally measure  $U$ ,  $V$ ,  $p$ ,  $T$ , and then integrate the above equation to obtain the function  $S(U, V)$ . You 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.

Historically, the most prominent effort of this kind has been to determine the function  $S(U, V)$  for water. The experimental results are presented as tables and contour plots. Even a cursory look at these tables and plots will give you an appreciation of the thoughts gone into presenting data in concise and useful ways.

Today, the function  $S(U, V)$  is available online for many substances. For example, NIST maintains a website, <http://webbook.nist.gov/chemistry/fluid/>.

**Thermodynamic model of the heat reservoir.** A heat reservoir maintains a fixed temperature  $T_R$ , and interacts with the rest of the world in only one manner: exchanging energy. When the energy of the reservoir varies by  $\delta U_R$ , the entropy of the reservoir varies by

$$\delta S_R = \frac{\delta U_R}{T_R}.$$

**Thermodynamic model of the weight.** The weight exerts on the piston a fixed force,  $f_{\text{weight}}$ . Now 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  $U_{\text{weight}}$  and a fixed entropy  $S_{\text{weight}}$ . That is,  $U_{\text{weight}}$  and  $S_{\text{weight}}$  are independent of the height of the weight,  $h$ . The potential energy of the weight is the force times the height, namely,

$$\text{potential energy of weight} = f_{\text{weight}} h.$$

The sum of the potential energy of the weight and the internal energy of the weight gives the total energy  $E_{\text{weight}}$  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  $\delta h$ , 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.

**Construct an isolated system with internal variables.** The half bottle of wine, the heat reservoir, 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 heat reservoir,  $T_R$ ,
- the force due to the weight,  $f_{\text{weight}}$ .

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,  $U_{\text{weight}}$ ,
- the entropy of the weight,  $S_{\text{weight}}$ .

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  $\delta V$  and the height of the weight changes by  $\delta h$ . The changes of the two geometric parameters are related as

$$\delta V = A \delta h,$$

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 law of the conservation of energy, the energy of the isolated system is constant, independent of the values of the internal variables, so that

$$\delta U + f_{\text{weight}} \delta h + \delta U_R = 0.$$

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

**Maximize the entropy of an isolated system as a function of internal variables.** The conservation of space and the conservation of energy place two constraints among the variations of the four internal variables,  $\delta U$ ,  $\delta V$ ,  $\delta h$ ,  $\delta U_R$ . Consequently, only two of the four are independent. We will take the energy of the wine  $U$  and the volume of the wine  $V$  to be the two independent internal variables. Thus, the composite—the wine, the weight and the heat reservoir together—is an isolated system with two independent internal variables: the energy of the wine  $U$  and the volume of the wine  $V$ .

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,  $p_{\text{weight}} = f_{\text{weight}} / A$ .

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  $\delta U$  and the volume of the wine varies by  $\delta V$ , the entropy of the composite varies by

$$\delta S_{\text{composite}} = \left[ \frac{\partial S(U, V)}{\partial U} - \frac{1}{T_R} \right] \delta U + \left[ \frac{\partial S(U, V)}{\partial V} - \frac{p_{\text{weight}}}{T_R} \right] \delta V.$$

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,

$$\delta S_{\text{composite}} = 0$$

for arbitrary small variations  $\delta U$  and  $\delta V$ .

Because  $\delta U$  and  $\delta V$  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:

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

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,  $S(U, V)$ .

In the above, we have regarded  $T_R$  and  $p_{\text{weight}}$  as fixed loading parameters. The above two equations are still valid when we place the wine on another heat reservoir of a different temperature, or under another weight with a different force, and wait for them to equilibrate. 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

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

These two equations constitute the *equations of state* of the wine once the function  $S(U, V)$  is known. The first equation recovers the definition of the temperature, and the second equation interprets the other partial derivative.

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

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

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

$$\delta S = \frac{1}{T} \delta U + \frac{p}{T} \delta V.$$

**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  $N$ th power of  $V$ :

$$\Omega \propto V^N.$$

The proportional factor will depend on  $U$  and  $N$ , but not on  $V$ .

By definition, the entropy is  $S = \log \Omega$ . Inserting the above expression for the number of quantum states into the equation of state involving the pressure,

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

we obtain that

$$\frac{p}{T} = \frac{N}{V}.$$

This is the familiar ideal gas law.

**Thermoelasticity of an ideal gas.** 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*.

As described above, an ideal gas satisfies

$$pV = NT.$$

It is also known that the energy of an ideal gas is given by

$$U = cNT,$$

where  $c$  is the heat capacity per molecule, and is taken to be a constant for a given species of molecules.

Inserting the above relations into the fundamental relation

$$\delta S = \frac{1}{T} \delta U + \frac{p}{T} \delta V,$$

we obtain that

$$\delta S = \frac{cN}{U} \delta U + \frac{N}{V} \delta V.$$

Integrating, we obtain that

$$S(U, V) = S(U_0, V_0, N) + cN \log\left(\frac{U}{U_0}\right) + N \log\left(\frac{V}{V_0}\right),$$

where  $U_0$  and  $V_0$  are arbitrary reference values. The number of quantum states is

$$\Omega(U, V) = \Omega(U_0, V_0, N) \left(\frac{U}{U_0}\right)^{cN} \left(\frac{V}{V_0}\right)^N.$$

**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  $\mu$ m, 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  $S = \log \Omega$  and the defining equation of the pressure,



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

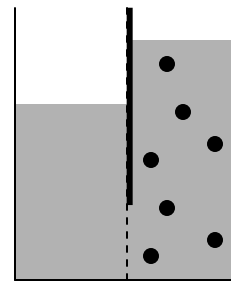
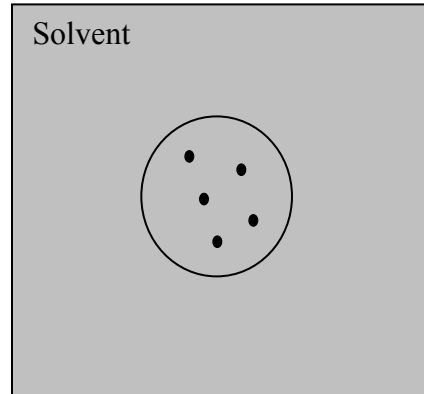
Inserting the expression  $\Omega \propto V^N$ , we obtain that

$$\frac{p}{T} = \frac{N}{V}.$$

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 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.



**Represent a thermodynamic state as a point in a plane.** We now return to the general discussion of a system capable of two independent variations,  $U$  and  $V$ . Consider a plane with  $U$  and  $V$  as the coordinates. 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 thermodynamic states, known as a *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.**

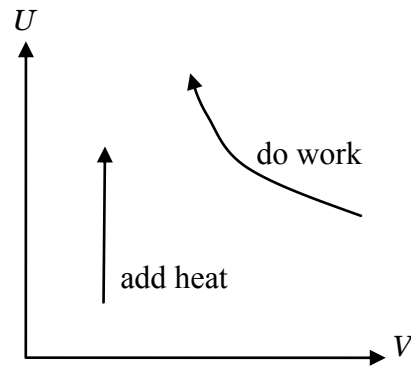
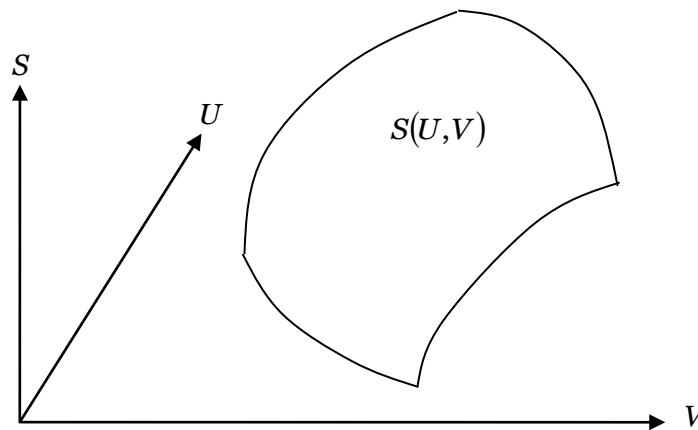
Following Gibbs, we represent the function  $S(U, V)$  as a surface in the three-dimensional space, with  $(U, V)$  as the horizontal plane, and  $S$  as the vertical axis. The volume  $V$  has absolute significance, but the energy  $U$  is significant up to an additive constant. We have set  $S = 0$  for the ground state.

Recall the equations of state:

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

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 and 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  $f_{\text{weight}}$  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  $p_{\text{weight}}/T_R$  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  $p_{\text{weight}}$ , 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:

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

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  $p_{\text{weight}}/T_R$ .

When the loads,  $1/T_R$  and  $p_{\text{weight}}/T_R$ , 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 small perturbation. Local maximization.** To ensure that the vertical distance  $S_{\text{composite}}(U, V)$  is maximized at  $(U, V)$ , the surface  $S(U, V)$  must be below the tangent plane—that is, the surface  $S(U, V)$  is convex at the state  $(U, V)$ . The condition for local maximization can be expressed in an analytic form.

When the state varies by  $\delta U$  and  $\delta V$ , the entropy of the composite varies by

$$\begin{aligned} \delta S_{\text{composite}} = & \left[ \frac{\partial S(U, V)}{\partial U} - \frac{1}{T_R} \right] \delta U + \left[ \frac{\partial S(U, V)}{\partial V} - \frac{p_{\text{weight}}}{T_R} \right] \delta V \\ & + \frac{\partial^2 S(U, V)}{2\partial U^2} (\delta U)^2 + \frac{\partial^2 S(U, V)}{\partial U \partial V} (\delta U)(\delta V) + \frac{\partial^2 S(U, V)}{2\partial V^2} (\delta V)^2 \end{aligned}$$

We have expanded the Taylor series of the function  $S(U, V)$  up to terms quadratic in  $\delta U$  and  $\delta V$ . In a state of equilibrium, the coefficients of the first-order variations vanish, recovering the equations of state. To ensure that this state of equilibrium maximizes  $S_{\text{composite}}$ , the sum of the second-order variations must be negative for arbitrary combination of  $\delta U$  and  $\delta V$ .

According to calculus, the cross derivatives of a function are independent the order of differentiation, namely,

$$\frac{\partial^2 S(U, V)}{\partial V \partial U} = \frac{\partial^2 S(U, V)}{\partial U \partial V}.$$

The matrix

$$\mathbf{H}(U, V) = \begin{bmatrix} \frac{\partial^2 S(U, V)}{\partial U^2} & \frac{\partial^2 S(U, V)}{\partial V \partial U} \\ \frac{\partial^2 S(U, V)}{\partial U \partial V} & \frac{\partial^2 S(U, V)}{\partial V^2} \end{bmatrix}$$

is known as the Hessian of the function  $S(U, V)$ .

A state of equilibrium is stable against arbitrary small perturbation in  $U$  and  $V$  if the Hessian,  $\mathbf{H}(U, V)$ , is negative-definite. According to linear algebra, the two-by-two matrix is negative-definite if and only if

$$\frac{\partial^2 S(U, V)}{\partial U^2} < 0, \quad \frac{\partial^2 S(U, V)}{\partial V^2} < 0, \quad \left[ \frac{\partial^2 S(U, V)}{\partial U^2} \right] \left[ \frac{\partial^2 S(U, V)}{\partial V^2} \right] > \left[ \frac{\partial^2 S(U, V)}{\partial U \partial V} \right]^2.$$

When the Hessian is negative-definite at a state  $(U, V)$ , the function  $S(U, V)$  is convex at this state.

**State of equilibrium stable against large perturbation. Global maximization.** If the surface  $S(U, V)$  is globally 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  $p_{\text{weight}}/T_R$ . 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  $p_{\text{weight}}/T_R$ .

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  $p_{\text{weight}}/T_R$  are related.

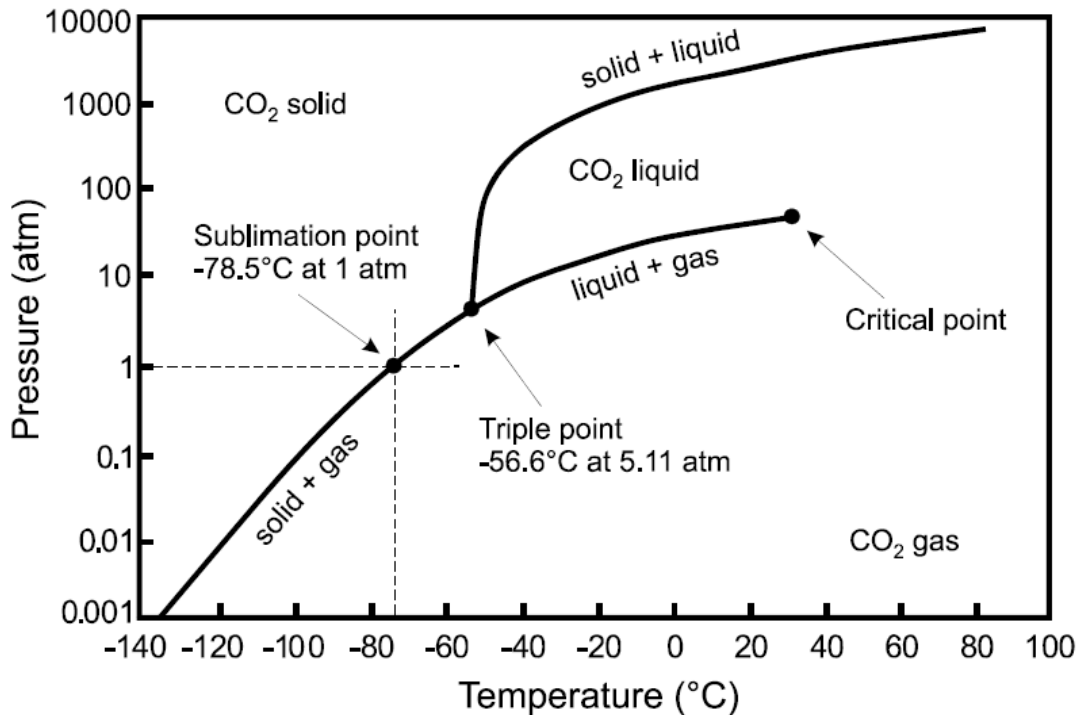
As the tangent plane touching the surface at two points rolls, the two points may merge to a single point. When the tangent plane is rolled beyond this special point, the tangent plane will touch the surface at only one point, and the tangent plane can be rolled with two degrees of freedom. This special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

**Phase diagram of a pure substance.** We have studied a phase transition of a substance by using a model of a system with a single independent variable: energy (<http://imechanica.org/node/4878>). 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.



Pressure-Temperature phase diagram for CO<sub>2</sub>.

A two-variable model will accommodate this experimental observation and many others. Some of the other observations are illustrated by a diagram on a  $(T, p)$  plane, known as a phase diagram of a 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.

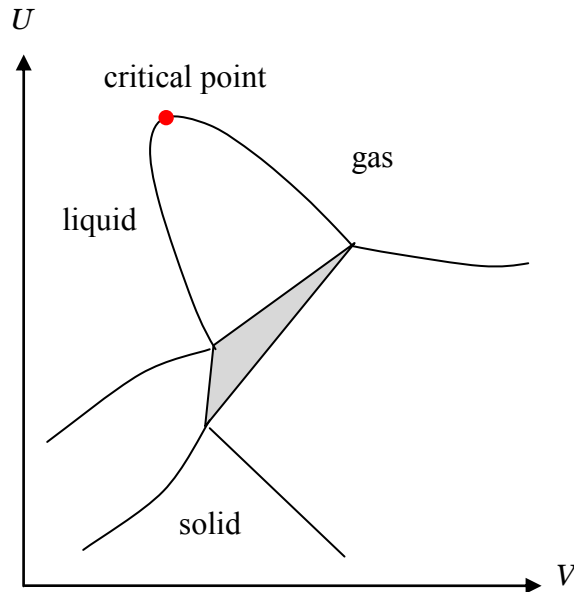
Between two neighboring regions is a curve, known as a *phase boundary*. When the temperature and the pressure fall on such a curve, two phases coexist.

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 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 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

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

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 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 function  $s'(u',v')$ , and the other by  $s''(u'',v'')$ . 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*.

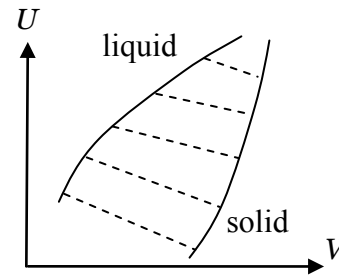
The rules of mixture have a simple graphical interpretation in the three-dimensional space of  $(S,U,V)$ . Given a function  $s'(u',v')$ , the set of points  $(Ns', Nu', Nv')$  is a surface, representing the substance when all molecules are in phase  $A'$ . Similarly, given a function  $s''(u'',v'')$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

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

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

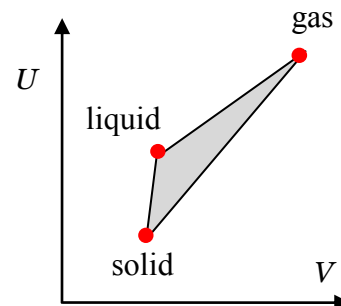
For the two phases to coexist, the composite—the system and the heat reservoir together—should have the same entropy in the two phases, namely,

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

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

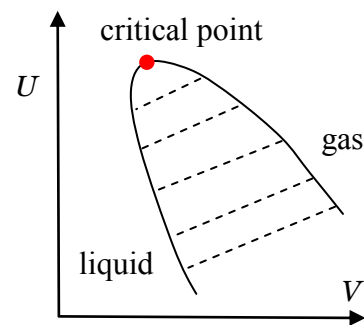
$$\begin{aligned} \frac{\partial s'(u', v')}{\partial u'} &= \frac{\partial s''(u'', v'')}{\partial u''} = \frac{\partial s'''(u''', v''')}{\partial u'''} \\ \frac{\partial s'(u', v')}{\partial v'} &= \frac{\partial s''(u'', v'')}{\partial v''} = \frac{\partial s'''(u''', v''')}{\partial v'''} \\ s'(u',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

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.

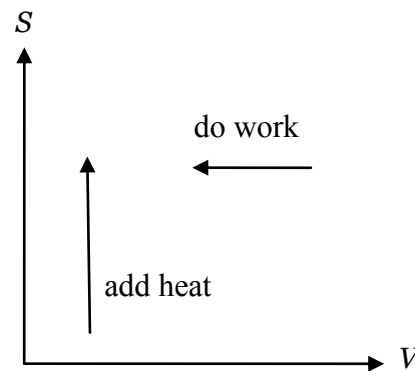
**A system with variable energy and volume, as well as an internal variable.** We return to general discussion to a system capable of two independent variations, the energy  $U$  and the volume  $V$ . In the case of the half bottle of wine, beside adding heat and doing work to the wine, we may be interested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

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 flipping in a set of quantum states. According to the fundamental postulate, all the quantum states are equally probable after the system is isolated for a long time. When the internal variable  $Y$  is fixed at a particular value, the system can only flip among a subset of the quantum states. The logarithm of the number of quantum states in this subset is  $S(U, V, Y)$ . When  $U$  and  $V$  are fixed, of all values of  $Y$ , the most probable value of  $Y$  maximizes the function  $S(U, V, Y)$ .

**Energy  $U(S, V)$ .** Consider a system characterized by a function  $S(U, V)$ . When the volume is fixed, the more energy a system has, the more quantum states the system has. Consequently, 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 real 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

$$U = U(S, V).$$

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 expression

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

Solving  $dU$ , 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

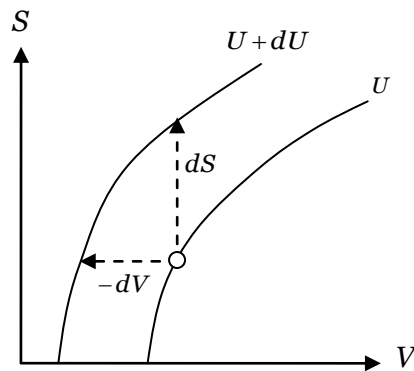
$$T = \frac{\partial U(S, V)}{\partial S}, \quad p = -\frac{\partial U(S, V)}{\partial V}.$$

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  $U(S, V)$ , while  $T$  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.

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, of all values of  $Y$ , the most probable value of  $Y$  minimizes the function  $U(S, V, Y)$ .

**Helmholtz function**  $F(T, V)$ . A system, such as a half bottle of wine, is characterized by energy  $U$  and volume  $V$ , as well as by an internal variable  $Y$ . The thermodynamics of the wine is specified by the function  $S(U, V, Y)$ . Now we consider a special case: the system is in thermal equilibrium with a heat reservoir of a fixed temperature  $T$ , so that

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

This equation defines the function  $T(U, V, Y)$ . If  $T$  is a monotonic function of  $U$ , this function can be inverted to obtain the function  $U(T, V, Y)$ .

Recall the following results from the lecture on function (<http://imechanica.org/node/4878>). Define the Helmholtz function

$$F = U - TS.$$

When  $(T, V)$  are fixed, of all values of  $Y$ , the most probable value of  $Y$  minimizes the function  $F(T, V, Y)$ .

When  $Y$  is held constant, taking differential of the function  $F = U - TS$ , we obtain that

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

Recall that  $dU = TdS - pdV$  when  $Y$  is held constant. The above equation becomes that

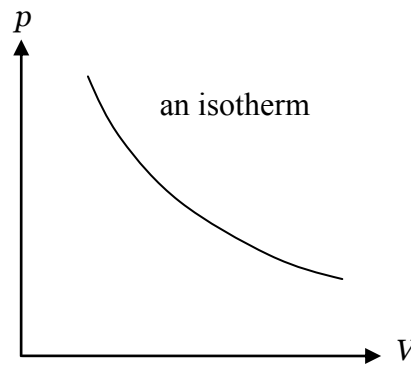
$$dF = -SdT - pdV.$$

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

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

**$(p, V)$  plane.** Thermodynamic states of the system can be represented on the  $(p, V)$  plane. A point in the plane represents a thermodynamic state, and a curve in the plane represents a loading path. Sketched in the plane is a pressure-

volume curve measured under the condition of a constant temperature. Such a loading path is known as an isotherm. The area under this curve determines the change in the Helmholtz function of the system when compressed under the isothermal condition.



**Second derivatives of the Helmholtz function.** Consider a system characterized by a Helmholtz function  $F(T, V)$ . The equations of states are

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

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

The equations of state are in general nonlinear, and can be linearized in the neighborhood of any particular thermodynamic state. According to calculus, we write

$$-\delta S = \frac{\partial^2 F(T, V)}{\partial T^2} \delta T + \frac{\partial^2 F(T, V)}{\partial V \partial T} \delta V,$$

$$-\delta p = \frac{\partial^2 F(T, V)}{\partial T \partial V} \delta T + \frac{\partial^2 F(T, V)}{\partial V^2} \delta V.$$

This procedure is known as linear perturbation, and the above two equations are the linearized equations of state.

The equations of state interpret the first derivatives of the function  $F(T, V)$ . The linearized equations of state interpret the second derivatives of the function  $F(T, V)$ .

Let us try to interpret  $\partial^2 F(T, V) / \partial T^2$ . The heat capacity is defined as

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

That is, the heat capacity is the change in energy of the system associated with a unit change in the temperature, while the volume of the system is held constant. The subscript indicates that the volume is held constant when the temperature changes. Recall that  $U = F + TS$ , so that

$$C_v = \frac{\partial F(T, V)}{\partial T} + S + T \frac{\partial S(T, V)}{\partial T}.$$

This equation becomes

$$C_v = -T \frac{\partial^2 F(T, V)}{\partial T^2}.$$

We next look at  $\partial^2 F(T, V) / \partial V^2$ . We may define stiffness by

$$\kappa_T = -V \frac{\partial p(T, V)}{\partial V}.$$

Comparing this definition with the second perturbed equation of state, we obtain that

$$\kappa_T = V \frac{\partial^2 F(T, V)}{\partial V^2}.$$

According to calculus, the cross derivatives of a function are independent of the order of differentiation, namely,

$$\frac{\partial^2 F(T, V)}{\partial V \partial T} = \frac{\partial^2 F(T, V)}{\partial T \partial V}.$$

The cross derivative measures the effect of thermomechanical coupling.

**Enthalpy**  $H(S, p)$ . When the weight and wine equilibrate, we can speak of the pressure of the wine,  $p$ , and write

$$p = -\frac{\partial U(S, V, Y)}{\partial V}.$$

This relation defines the function  $p(S, V, Y)$ . When  $S$  is fixed, assuming  $p$  and  $V$  are 1-to-1, we can invert the function  $p(S, V, Y)$  to obtain the function  $V(S, p, Y)$ .

The energy of the combination of the wine and the weight is

$$H = U + pV.$$

The quantity  $H$  is known as the *enthalpy* of the wine. The terminology is clearly unfair to the weight. The enthalpy is a function of  $S$  and  $p$ . When  $(S, p)$  are fixed, of all values of  $Y$ , the most probable value of  $Y$  minimize the function  $H(S, p, Y)$ .

When  $Y$  is held constant, taking differential of  $H = U + pV$ , we obtain that

$$dH = dU + p dV + V dp.$$

Recall that  $dU = T dS - p dV$  when  $Y$  is held constant. The above equation becomes that

$$dH = T dS + V dp.$$

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

$$T = \frac{\partial H(S, p, Y)}{\partial S}, \quad V = \frac{\partial H(S, p, Y)}{\partial p}.$$

**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  $G(T, p)$ .

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

In physical terms, this change of variables means that the system can change both energy and volume, but not particles. One can similarly state the condition of equilibrium. When a system is held at fixed temperature and pressure, upon lifting a constraint internal to the system, after a long time, the more probable value of the internal variable has a smaller value of the Gibbs function.

**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  $\text{CO}_2$  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  $A''$ .



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

**Exercise.** Along a two-phase boundary, show that

$$\frac{dp}{dT} = \frac{s'' - s'}{v'' - v'}$$

**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?

**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.

**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.

**Optional reading.** T.D. Wheeler, A.D. Stroock, The transpiration of water at negative pressure in a synthetic tree. *Nature* 455, 208-212.

**Optional reading.** K.Z. House, D.P. Schrag, C.F. Harvey, K.S. Lackner. Permanent carbon dioxide storage in deep-sea sediments. *PNAS* 103, 12291-12295 (2006).

## References

- J.W. Gibbs, Graphical methods in the thermodynamics of fluids. *Trans. Conn. Acad.* 11, 309-342, 1873. This paper and the next one are collected in the *Scientific Papers of J. Willard Gibbs*, freely available online at Google Books. These seminal papers have remained the cleanest treatment of systems of two independent variables. The serious student of thermodynamics should read them with care.
- J.W. Gibbs, A method of graphical representation of the thermodynamic properties of substances by means of surfaces. *Trans. Conn. Acad.* 11, 382-404, 1873.
- T. Andrews, On the continuity of the gaseous and liquid states of matter, *Philosophical Transactions of the Royal Society of London* 159, 575-590 (1869).

- H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2<sup>nd</sup> edition, John Wiley & Sons, Inc., New York, 1985.

**Engineering thermodynamics.** Texts used by undergraduate students in mechanical engineering contain detailed descriptions of thermodynamic properties of pure substances.

- C. Borgnakke and R.E. Sonntag, *Fundamentals of Thermodynamics*, 7<sup>th</sup> edition, Wiley, 2009.
- Y.A. Cengel and M.A. Boles, *Thermodynamics*, 7<sup>th</sup> edition, McGraw Hill, 2010.
- M.J. Moran, H.N. Shapiro, D.D. Boettner and M.B. Bailey, *Fundamentals of Engineering Thermodynamics*, 7<sup>th</sup> edition, 2011.

**Appendix A: Linearized equations of state.** A system, such as a half bottle of wine, is modeled by a function  $S(U, V)$ . Once the function  $S(U, V)$  is prescribed, the equations of state are

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

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

The system is in equilibrium with a weight and a heat reservoir. The above equations of state suggest that we may regard  $1/T$  and  $p/T$  as the loading parameters, and use  $U$  and  $V$  to specify thermodynamic states. Given a pair of the loading parameters, the equations of state are algebraic equations that determine the thermodynamic state  $(U, V)$ .

The equations of state are in general nonlinear algebraic equations. If the system is in the neighborhood of a particular thermodynamic state  $(U, V)$ , the equations of state can be linearized in this neighborhood, written in an incremental form:

$$\delta\left(\frac{1}{T}\right) = \frac{\partial^2 S(U, V)}{\partial U^2} \delta U + \frac{\partial^2 S(U, V)}{\partial V \partial U} \delta V,$$

$$\delta\left(\frac{p}{T}\right) = \frac{\partial^2 S(U, V)}{\partial U \partial V} \delta U + \frac{\partial^2 S(U, V)}{\partial V^2} \delta V.$$

The increments of the loads,  $\delta(1/T)$  and  $\delta(p/T)$ , are linear in the increments of  $\delta U$  and  $\delta V$ . This procedure is known as linear perturbation, and the above two equations are the linearized equations of state.

A thermodynamic state of the wine can be represented by a point in the

$(U, V)$  plane, as well as by a point in the  $(p, T)$  plane. For the same state of the system, the point in the  $(U, V)$  plane is mapped to the point in the  $(p, T)$  plane by the equations of state. The mapping may not always be invertible. That is, given a pair of the loads  $(p, T)$ , the equations of state may not be invertible to determine a pair  $(U, V)$ . For example, the perturbed equations of state are not invertible when the Hessian is a singular matrix,

$$\det \mathbf{H} = 0.$$

This singularity may be understood in terms of thermodynamics.

**Appendix B: Legendre transformation.** In the body of the text we have changed variables many times. Some of the changes of variable can be done by a mathematical procedure known as the *Legendre transformation*. We illustrate this procedure as follows.

Start with a function

$$U = U(S, V),$$

and the symbols we give to its partial derivatives

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

Thus, the small changes are related as

$$dU = TdS - pdV.$$

Define a function by

$$H = U + pV.$$

For small changes in the variables, we obtain that

$$dH = dU + d(pV).$$

Recall  $dU = TdS - pdV$  and an identity in calculus  $d(pV) = pdV + Vdp$ . We obtain that

$$dH = TdS + Vdp.$$

Consequently,  $H$  is a function of  $S$  and  $p$ . The coefficients in the differential form can be defined by partial derivatives of the function  $H(S, p)$ :

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

In this example, the Legendre transformation replaces  $V$  by  $p$  as an independent variable.

**Appendix C: Maxwell relations.** Recall an identity in calculus: given a differential function  $f(x,y)$ , the partial derivatives are indifferent to the order by which they are taken. Thus,

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

Applying this identity to the two variables in the function  $U(S,V)$ , we obtain that

$$\frac{\partial^2 U(S,V)}{\partial S \partial V} = \frac{\partial^2 U(S,V)}{\partial V \partial S},$$

or

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

This equation is known as a Maxwell relation. The procedure can be applied to any other functions.

The significance of the relation can be appreciated as follows. When the entropy varies by  $\delta S$  and the volume varies by  $\delta V$ , the temperature and the pressure varies by

$$\begin{aligned} \delta T &= \frac{\partial T(S,V)}{\partial S} \delta S + \frac{\partial T(S,V)}{\partial V} \delta V \\ -\delta p &= -\frac{\partial p(S,V)}{\partial S} \delta S - \frac{\partial p(S,V)}{\partial V} \delta V. \end{aligned}$$

Thus, the variations  $(\delta T, -\delta p)$  are linear in the variations  $(\delta S, \delta V)$ . The Maxwell relation ensures that the mapping matrix is symmetric.

**Appendix D: Analysis of two phases in equilibrium.** When the internal variables vary, the total number of molecules  $N$  in the mixture is conserved, so that

$$dN' + dN'' = 0.$$

Similarly, the total energy in the mixture  $U$  is conserved, so that

$$u' dN' + N' du' + u'' dN'' + N'' du'' = 0.$$

The total volume of the mixture  $V$  is conserved, so that

$$v' dN' + N' dv' + v'' dN'' + N'' dv'' = 0.$$

The three laws of conservation place three constraints among the six variations  $dN'$ ,  $dN''$ ,  $du'$ ,  $du''$ ,  $dv'$ ,  $dv''$ .

When the internal variables vary, the entropy of the mixture  $S = N's'(u',v') + N''s''(u'',v'')$  varies by

$$dS = N' \frac{ds'(u')}{du'} du' + s'(u') dN' + N'' \frac{ds''(u'')}{du''} du'' + s''(u'') dN''$$

We regard  $dN'$  and  $du'$  as independent variations, and eliminate  $dN''$  and  $du''$  by using the laws of conservation. The variation in entropy is

$$\begin{aligned} dS = & N' \left[ \frac{\partial s'(u', v')}{\partial u'} - \frac{\partial s''(u'', v'')}{\partial u''} \right] du' \\ & + N' \left[ \frac{\partial s'(u', v')}{\partial v'} - \frac{\partial s''(u'', v'')}{\partial v''} \right] dv' \\ & + \left[ s'(u', v') - s''(u'', v'') - (u' - u'') \frac{\partial s''(u'', v'')}{\partial u''} - (v' - v'') \frac{\partial s''(u'', v'')}{\partial v''} \right] dN' \end{aligned}$$

When the two phases equilibrate in the mixture, the entropy is maximized. Because  $du'$ ,  $dv'$  and  $dN'$  are independent variations, the factor in front of each variation must vanish, giving

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

These three equations recover the graphic representation. Once the fundamental thermodynamic functions of the two phases,  $s'(u', v')$  and  $s''(u'', v'')$  are prescribed, these are three nonlinear algebraic equations involving four unknowns:  $u'$ ,  $u''$ ,  $v'$ ,  $v''$ . Consequently, for a substance characterized by two independent variations, when two phases of the substance coexist, the mixture can still have one independent variation.