CHEMICAL POTENIAL

A system capable of three independent variations. Once again we regard a half glass of wine as a system. It is a rather complex system. In particular, the system is a mixture of two phases: liquid and gas. Both phases are included when we refer to "the wine". The system contains many species of molecules—water, ethanol, etc.
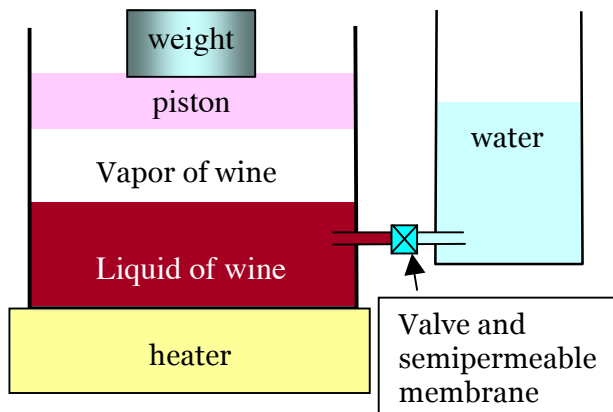
We arrange to vary the system in three ways. We change the volume of the system by moving a piston using a weight, add matter to the system by opening a valve that connects to a cup of water, and transfer heat to the system by bringing the wine into thermal contact with a heater.

There may be other ways to do work to the wine, but we will neglect them for now. There are many species of molecules in the wine; we will use a valve equipped with a *semi-permeable membrane*, which allows water molecules to go through, but blocks all other species of molecules. Consequently, of all species of molecules in the wine, only the number of water molecules can vary.

We model the wine as a system with three independent variables:

- the energy in the wine, U
- the volume occupied by the wine, V
- the number of water molecules in the wine, N

The volume of the wine is varied by moving the piston, and the number of water molecules in the wine is varied by opening the valve. The energy of the wine, however, is varied by all three ways—moving the piston, opening the valve, and contacting the heater. We regard U, V, N as *independent* variables. When we hold any two constant, we can still vary the third one.

The function $S(U,V,N)$ of a system. When we thermally insulate the wine, fix the position of the piston, and close the valve, the three variables of the wine, (U,V,N), are fixed at a particular set of values. Consequently, once (U,V,N) are fixed, the wine is an isolated system, flipping among a set of microstates. Let Ω be the number of the microstates of the isolated system.

When the three variables (U, V, N) are fixed at a different set of values, the wine becomes another isolated system, flipping among another set of microstates. Consequently, the wine with the three variables corresponds to a family of isolated systems, and the number of microstates is a function of the three variables:

$$\Omega(U, V, N).$$

We call the quantity $\log \Omega$ the entropy, and give it a symbol S, namely,

$$S = \log \Omega.$$

The logarithmic function is introduced to simplify mathematics. We make the composite of the wine and the cheese as an isolated system. The number of microstates of the composite is the number of microstates of the wine times the number of microstates of the cheese. The logarithmic function converts this multiplication to an addition: the entropy of the composite is the sum of the entropy of the wine and the entropy of the cheese.

For a system with three variables (U, V, N), the entropy of the system is a function of the three variables, namely,
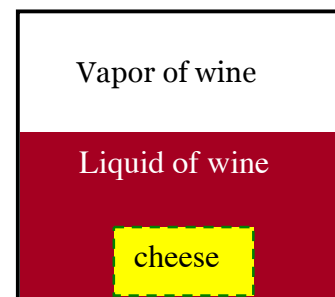
$$S = S(U, V, N).$$

Two systems exchanging energy, space, and matter. Now consider two systems: a glass of wine and a piece of cheese. Both systems contain water. When the wine and cheese are nearby, water molecules may escape from the wine, and then enter the cheese. Of course, water molecules may go the other way around, from the cheese to the wine. How do we predict the direction of water transfer without placing them together? That is, how do we know which one is wetter, the wine or the cheese?

The two systems, the wine and the cheese, are designated as A' and A''. They are characterized by different functions, $S'(U', V', N')$ and $S''(U'', V'', N'')$. We make the composite of the wine and the cheese into an isolated system, so that the sums,

$$U' + U'', \ V' + V'', \ N' + N'',$$

are *fixed* as the wine and the cheese exchange energy, volume, and water. The cheese is wrapped with a semi-permeable membrane, so that cheese and the wine can exchange water molecules, but not any other species of molecules.

The composite has three independent internal variables: the partitions of energy, volume, and water between the wine and the cheese. A

particular set of partitions defines a *macrostate* of the composite. For a given set of partitions of energy, volume, and water between the wine and the cheese, the two systems are two isolated systems, each flipping among a set of microstates. A microstate of the wine and a microstate of the cheese together constitute a microstate of the composite. The number of microstates of the composite under this set of partitions is the product of the number of microstate of the wine and that of the cheese. Consequently, the entropy of the composite under this set of partitions is the sum of the entropies of the wine and the cheese:

$$S_{com} = S'(U',V',N') + S''(U'',V'',N'').$$

The composite changes from one macrostate to another as the wine and the cheese exchange energy, volume, and water. When the wine changes energy by δU, changes volume by δV, and changes the number of water molecules by δN, the cheese changes energy by $-\delta U$, changes volume by $-\delta V$ and changes the number of water molecules by $-\delta N$. Associated with this change of the three internal variables, the composite changes its macrostate, and the entropy of the composite changes by

$$\delta S_{com} = \left[\frac{\partial S'(U',V',N')}{\partial U'} - \frac{S''(U'',V'',N'')}{\partial U''}\right]\delta U$$
$$+ \left[\frac{\partial S'(U',V',N')}{\partial V'} - \frac{S''(U'',V'',N'')}{\partial V''}\right]\delta V$$
$$+ \left[\frac{\partial S'(U',V',N')}{\partial N'} - \frac{S''(U'',V'',N'')}{\partial N''}\right]\delta N$$

According to the fundamental postulate, any change of the internal variables of an isolated system will increase the entropy of the isolated system (http://imechanica.org/node/290). That is, for any combination of δU, δV and δN,

$$\delta S_{com} \geq 0.$$

This inequality may be satisfied in many ways. We next describe two examples.

Equilibrium between two systems exchanging energy, space, and matter. For any combination of δU, δV and δN, the equality

$$\delta S_{com} = 0$$

holds when the wine and the cheese are in equilibrium. Consequently, upon exchanging energy, volume and water molecules, the two systems equilibrate when

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

$$\frac{\partial S'\left(U',V',N'\right)}{\partial V'} = \frac{S''\left(U'',V'',N''\right)}{\partial V''},$$

$$\frac{\partial S'\left(U',V',N'\right)}{\partial N'} = \frac{S''\left(U'',V'',N''\right)}{\partial N''}.$$

The two functions, $S'\left(U',V',N'\right)$ and $S''\left(U'',V'',N''\right)$, are taken to be known. Once the total energy, volume and number of water molecules are given, the above conditions of equilibrium are nonlinear algebraic equations that determine the *equilibrium partitions* of the energy, volume and water between the two systems.

Partial equilibrium between two systems exchanging energy, space, and matter. The composite has many ways vary its macrostates to *increase* its entropy. For example, the wine and the cheese may redistribute energy and volume rapidly. However, the cheese is wrapped by a semi-impermeable membrane that allows water molecules to go through very slowly. Consequently, the wine and the cheese are in partial equilibrium with respect to exchanging energy and volume, but are not in equilibrium with respect to exchanging water. In this example, the inequality $\delta S_{com} \geq 0$ becomes three separate conditions:

$$\frac{\partial S'\left(U',V',N'\right)}{\partial U'} = \frac{S''\left(U'',V'',N''\right)}{\partial U''},$$

$$\frac{\partial S'\left(U',V',N'\right)}{\partial V'} = \frac{S''\left(U'',V'',N''\right)}{\partial V''},$$

$$\left[\frac{\partial S'\left(U',V',N'\right)}{\partial N'} - \frac{S''\left(U'',V'',N''\right)}{\partial N''}\right]\delta N > 0.$$

When the energy, the volume, and the number of water molecules are at a specific set of partitions, all the partial derivatives are known. According to the last condition, if

$$\frac{\partial S'\left(U',V',N'\right)}{\partial N'} > \frac{S''\left(U'',V'',N''\right)}{\partial N''},$$

to increase the entropy of the composite, the wine gains water from the cheese, namely, $\delta N > 0$. Conversely, if

$$\frac{\partial S'\left(U',V',N'\right)}{\partial N'} < \frac{S''\left(U'',V'',N''\right)}{\partial N''},$$

to increase the entropy of the composite, the wine loses water to the cheese, namely, $\delta N < 0$. At the end of the notes, we will convert the inequality into an equation by using a kinetic model.

Name partial derivatives of the function $S(U,V,N)$ of a system.

It is too much work to write these partial derivatives all the time. We will give each partial derivative some kind of shorthand. For a system of variable energy, volume and amount of water, the entropy of the system is a function of the three variables, namely,

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

When the independent variables change by small amounts, δU, δV and δN, the entropy changes by

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

We have interpreted one partial derivative by using the temperature *T*, namely,

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

See notes on Temperature (http://imechanica.org/node/291). Thus $1/T$ is the change in the entropy associated with unit change in the energy, while fixing the volume and the number of water molecules. The experimental significance of the temperature is as follows. When *V* and *N* are fixed, and the system is in contact with a reservoir of energy, energy goes from the system to the reservoir if the temperature of the system is higher than the temperature of the reservoir.

We have also interpreted another partial derivative by writing

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

See notes on Pressure (http://imechanica.org/node/885). Thus p/T is the change in the entropy associated with unit change in the volume, while fixing the energy and the number of water molecules. The experimental significance of the quantity p/T is as follows. When *U* and *N* are fixed, and the system is in contact with the reservoir of space, the volume of the system increases at the expense of the volume of the reservoir if the system has a higher value of p/T than the reservoir. In this experiment, only the partial derivative $\partial S(U,V,N)/\partial V$ has significance. For historical reasons, however, we give no distinct name to this partial derivative. Rather, we give two separate quantities: the pressure *p* and the temperature *T*. Of course, this single experiment is incapable of distinguish two quantities. The two quantities become separately meaningful when we open the system in two ways, changing both its energy and volume. That *p* is the same as the pressure used in mechanics will be clear when we discuss the function $U(S,V,N)$.

By analogy, we interpret yet another partial derivative by writing

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

The symbol μ is called the *chemical potential*. Thus μ/T is the change in the entropy associated with adding one water molecule to the system, while fixing the energy and the volume. When U and V are fixed, and the system is in contact with the reservoir of water molecules, water goes from the system to the reservoir if the system has a higher value of μ/T than the reservoir. Once again, in such an experiment, only the quantity μ/T is significant. To give μ a separate experimental interpretation, we will have to open the system in more than one way. In any event, the experiment of fixing U and V and then varying N is rather unusual. We will talk about other experimental conditions shortly.

We can also interpret the negative sign in the above definition. When two systems are in mechanical and thermal equilibrium, but not in equilibrium with respect to exchanging water, the following inequality holds:

$$\left[\frac{\partial S'(U',V',N')}{\partial N'} - \frac{S''(U'',V'',N'')}{\partial N''}\right]\delta N' > 0.$$

Rewrite the inequality as

$$-\left(\frac{\mu'}{T} - \frac{\mu''}{T}\right)\delta N' > 0$$

That is, the two systems have different chemical potentials of water, and water goes from the system with higher chemical potential of water to the system with a lower chemical potential.

Exercise. A half glass of wine and a piece of cheese can exchange energy, water and ethanol. The change of volume in either system is negligible. Develop the conditions that determine the directions of the exchange.

Temperature vs. chemical potential. The temperature of a system measures the change in the entropy of the system associated with the change in energy. We measure temperature by using a thermometer, and adding energy to the system by using a heater. Energy flows from a place of high temperature to a place of low temperature. Temperature corresponds to the daily experience of hotness. Indeed, our daily experience of hotness is so pervasive that it may even impede our learning of thermodynamics. It takes significant effort for us to sort out, of all our feelings for hotness, what is essential and what is incidental. Only then we can link our daily experience of hotness to the thermodynamics of temperature. See notes on Temperature (http://imechanica.org/node/291).

The chemical potential of ethanol in a glass of wine measures the change in the entropy of the wine associated with the change in the number of molecules of ethanol. Ethanol goes from a place of high chemical potential to a place of low chemical potential. Chemical potential corresponds to the daily experience of the smell of the wine.

Given similarly pervasive roles of temperature and chemical potential in our lives, we may wonder why we do not have the same level of familiarity with the two quantities. I can think of two reasons: one is cultural and the other technical. The cultural reason has to do with what our parents tell us. When we touch hot water, our parents tell us that the temperature of water is high. When we smell a strong wine, however, our parents miss the teachable moment, and fail to tell us that the chemical potential of ethanol is high. The phrase—the chemical potential of ethanol—is simply not in the everyday language. So blame our parents.

The technical reason is that, when we feel that something is hot, we attribute the sense of hotness to a single quantity: temperature. However, when we smell something, we may sense multiple quantities: a list of chemical potentials of a list of species of molecules. It is simpler to deal with one quantity than deal with multiple quantities. So blame our world: it confuses us with too many species of molecules.

Of all species of molecules, water is particularly significant to us. Our parents do tell us about humidity. Indeed, our experience of humidity can be mapped to the thermodynamics of the chemical potential of water, just as our experience of hotness can be mapped to the thermodynamics of temperature.

In everyday language, some of us may say that a wine is concentrated with alcohol when we feel a strong smell. Indeed, we will show that the concentration of a solute in a solution can be mapped to the chemical potential of the solute in the solution.

Thermodynamics 0, 1, 2, 3. In teaching thermodynamics, I have followed the following sequence:

- Isolated system (http://imechanica.org/node/290): a system capable of no variation. Entropy, S.
- Temperature (http://imechanica.org/node/291): a system capable of one independent variation. Entropy is a function of energy, $S(U)$.
- Pressure (http://imechanica.org/node/885): a system capable of two independent variations. Entropy is a function of energy and volume, $S(U,V)$.

- Chemical potential: a system capable of three independent variations. Entropy is a function of energy, volume and the number of water molecules, $S(U,V,N)$.

The word "entropy" is the shorthand for the phrase "the logarithm of the number of quantum states". Thermodynamics stands on a single fundamental postulate: A system isolated for a long time can be in any one of its quantum states with equal probability.

We can speak of the number of quantum states only for an isolated system, but we are interested in interactive systems. To study an interactive system in terms of an isolated system, we allow the system to vary quantities such as energy, volume, and the number of water. These quantities share a remarkable property: each is conserved. When the system loses energy, the rest of the world gains the same amount of energy.

Such an open system is characterized by the entropy as a function of the conserved quantities. When two systems exchange these conserved quantities, the composite of the two systems is an isolated system. The fundamental postulate ascribes experimental significance to the derivative of the entropy with respect to each of the conserved quantities. Given a system, we can measure its temperature, pressure, and chemical potential of water by equilibrating the system with another system with known temperature, pressure, and chemical potential of water.

Experimental determination of the function $S(U,V,N)$ **of a system**. For a given system of the three independent variables, we can determine the function $S(U,V,N)$ experimentally as follows. According to the above definitions, when the independent variables change by small amounts δU, δV and δN, the entropy changes by

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

We can put this system in contact with a reservoir, so that the system and the reservoir can exchange energy, volume, and water. When the system and the reservoir equilibrate, the values of T, p and μ of the system equal those of the reservoir. We have already known how to determine T and p by experiments. Once we know how to determine μ by experiments, we can use the above equation to determine the function $S(U,V,N)$ incrementally. We will describe the procedure to determine the chemical potential shortly.

Of course, you can always try to theoretically count the number of quantum states of the system, $\Omega(U, V, N)$, and calculate the entropy by $S = \log \Omega$. Such a theoretical counting can be done for a few idealized systems, and will not be pursued in this course.

Experimental determination of the chemical potential of a species of molecules in a complex system. How do we experimentally measure the chemical potential of a species of molecules in a complex system? When two systems can exchange energy and a species of molecules, the fundamental postulate dictates that the two systems reach equilibrium when they have the same temperature and the same chemical potential of the species of molecules. Consequently, once the chemical potential of a species of molecules in one system is determined, the system can be used to determine the chemical potential of the same species of molecules in other systems.

For example, as described in the next paragraph, we can determine the chemical potential of water molecules in a flask containing a pure water vapor as a function of temperature and pressure, $\mu = \mu(T, p)$. We now wish to measure the chemical potential of water molecules in the half glass of wine. We can bring the wine into contact with a flask of water vapor. The contact is made with a semi-permeable membrane that allows water molecules to go through, but blocks all other species of molecules. We then allow the wine to equilibrate with the water vapor in the flask, so that both energy and water molecules stop exchanging between the wine and the flask. The two systems have the same temperature and the same chemical potential. A reading of the chemical potential of water in the flask gives the chemical potential of water in the wine.

Chemical potential of a species of molecules in a pure substance. A pure substance aggregates a large number of a single species of molecules. Several basic phenomena of a pure substance, such as transition of phases and critical point, have been discussed in the notes on Pressure (http://imechanica.org/node/885). We now wish to determine the chemical potential of the species of molecules aggregated in the substance.

When the substance is in a single phase, the energy of a piece of the substance, *U*, is proportional to the number of molecules in the piece, *N*. Let the energy per molecule in the piece be

$$u = \frac{U}{N}.$$

The energy per molecule, *u*, is independent of the size and the shape of the piece. We can similarly define the entropy per molecule,

$$s = \frac{S}{N},$$

and the volume per molecule,

$$v = \frac{V}{N}.$$

For example, for a gas in a flask, V is the volume of the flask, so that v is much larger than the size of a molecule itself.

As a thermodynamic model of the substance, we prescribe the function

$$s = s(u,v).$$

The partial derivatives of the function are interpreted as

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

When the energy varies by δu and the volume varies by δv, the entropy varies by

$$\delta s = \frac{\delta u}{T} + \frac{p\,\delta v}{T}.$$

In the above equation, all the quantities on the right-hand side can be measured experimentally. Consequently, the function $s(u,v)$ can be determined by experiments for any pure substance.

Once the function $s(u,v)$ for a pure substance is determined, this function can be used to calculate all other thermodynamic functions, such as enthalpy and free energy. We now calculate the chemical potential of the species of the molecules in the substance. For a piece of a pure substance containing N molecules, the entropy, energy and volume of the piece are all proportional to N, namely,

$$S = Ns, \quad U = Nu, \quad V = Nv.$$

Once the substance is characterized by the function $s(u,v)$, the function $S(U,V,N)$ for the piece of the substance is given by

$$S(U,V,N) = Ns(u,v),$$

with

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

Recall the definition of the chemical potential:

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

Apply the chain rule in calculus, and we obtain that

$$\mu = -Ts - NT\frac{\partial s(u,v)}{\partial u}\left(-\frac{U}{N^2}\right) - NT\frac{\partial s(u,v)}{\partial v}\left(-\frac{V}{N^2}\right).$$

Simplifying, we find the chemical potential of a species in a pure substance:

$$\mu = -Ts + u + pv.$$

Once the function $s(u,v)$ for a pure substance is determined, so is the chemical potential of the species of the molecules that constitute the substance. Of all five quantities on the right-hand side of the above equation, only the energy u has an arbitrary additive constant. The same additive constant appears in the chemical potential. Incidentally, the right-hand side of the above equation happens to be the Gibbs free energy per molecule of the pure substance.

For many pure substances, the experimentally measured values of s, u and v are tabulated for various T and p. From the above equation, we can obtain the chemical potential of a molecular species in a pure substance as a function of the pressure and temperature

$$\mu = \mu(T, p).$$

Recall an old relation:

$$\delta s = \frac{\delta u}{T} + \frac{p\,\delta v}{T}.$$

A combination of the above two equations gives

$$\delta\mu = -s\,\delta T + v\,\delta p.$$

We interpret the partial derivatives of the function as

$$\frac{\partial\mu(T,p)}{\partial T} = -s, \quad \frac{\partial\mu(T,p)}{\partial p} = v.$$

In the above, we have considered a pure substance in a single phase. When two phases of the pure substance are in equilibrium with each other, the chemical potential of the species of molecules in the two phases are equal. For example, when liquid water equilibrates with its own vapor, the chemical potential of water in the liquid equals the chemical potential of water in the vapor.

Ideal gas. An ideal gas, of N number of a single species of molecules, and in a flask of volume V, is subject to pressure p and temperature T. Recall the ideal gas law

$$pV = NT.$$

The volume of the flask divided by the number of molecules is denoted by

$$v = V/N,$$

so that the ideal gas law becomes

$$pv = T.$$

Inserting the ideal gas law into the expression

$$\delta\mu = v\,dp,$$

and then integrating at a constant temperature, we obtain that

$$\mu(T,p) = \mu(T,p_o) + T\log(p/p_o).$$

At a fixed temperature, this expression determines the chemical potential of an ideal gas up to an additive constant.

For a mixture of several species of molecules, the above equations hold for each species, with the pressure interpreted as the partial pressure of the species. Thus, by changing the partial pressure of the species of molecules in a gas of multiple species of molecules, we can vary the chemical potential of the species in the gas.

Exercise. The gravity of the Earth pulls molecules of gas toward the Earth, by the entropy of the gas disperses the molecules into the space. Assume that the temperature is constant, how does the density of a species of molecules in the gas change with the elevation?

Pressures of water vapor in equilibrium with liquid water at several temperatures

T (C)	T (10^{-2} eV)	1/T (1/eV)	p (kPa)
0	2.36	42.4	0.61
10	2.45	40.8	1.23
20	2.52	39.7	2.34
30	2.61	38.3	4.24
40	2.70	37.0	7.38
50	2.79	35.8	12.33
100	3.22	31.1	101.33
37	2.68	37.3	6.28

Humidity. At a given temperature, when the air is in equilibrium with the liquid water, we say that the air is saturated with water. If a given volume of air contains fewer water molecules, the number of water molecules in the air divided by the number of water molecules in the saturated vapor is called the relative humidity (RH):

$$\text{RH} = \frac{N}{N_{satu}}.$$

When the vapor is modeled as an ideal gas, the relative humidity is also given by

$$\text{RH} = \frac{p}{p_{satu}},$$

where p is the partial pressure of water in the unsaturated gas, $p < p_{satu}$. We write the chemical potential of water in the air as

$$\mu = T \log\left(\frac{p}{p_{satu}}\right),$$

with the understanding that the chemical potential is relative to that of the water molecules in a saturated water at the same temperature.

The lung is always saturated with water vapor at the body temperature (37C), but the atmospheric air may not be. In winter, the cold air outside has low water content even at 100% relative humidity. When the cold air enters a warm room, the relative humidity in the room will reduce below 100% at the room temperature. We will feel uncomfortable. Also, water inside the warm room will condense on cold window panes.

Incompressible liquid. In many applications of liquids, the pressure is relatively small, so that the volume per molecule, v, is taken to be independent of the pressure. The chemical potential is

$$\mu(p) = \mu(0) + pv.$$

Thus, the chemical potential of a species of molecules in an incompressible liquid is linear in the pressure.

The function $U(S,V,N)$. When V and N are fixed, the entropy is an increasing function of energy: the more energy a system has, the more microstates the system has. Consequently, we can invert the function $S = S(U,V,N)$, and obtain the function

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

The two functions $S(U,V,N)$ and $U(S,V,N)$ contain the same information and characterize the same system capable of three independent variations. We have merely changed independent variables.

Recall the relation

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

Solving for δU, we find that

$$\delta U = T\delta S - p\delta V + \mu\delta N .$$

This equation was used by Gibbs to define the chemical potential. Consequently, the temperature, the pressure, and the chemical potential relate to partial derivatives of the function $U(S,V,N)$, namely,

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

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

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

In particular, the chemical potential of water in a system is the increase in the energy of the system when the system gains one water molecule, while *S* and *V* are fixed. The chemical potential has the unit of energy.

This definition gives the impression that *T*, *p* and *μ* are on a similar footing. But this impression has no fundamental significance: there is no reason to believe that $\partial U(S,V,N)/\partial N$ is more basic than $\partial S(U,V,N)/\partial N$. In choosing to name the former but not the latter, we have twisted our presentation to conform to Gibbs's preference.

Other choices of independent variables. For a system capable of three independent variations, we can choose quantities other than *U*, *V*, *N* as independent variables. Such a change of variables will help us to answer a question like, How does the number of molecules in the gas phase change when we open the valve, while keeping the volume and the temperature of the wine unchanged? Let us first see how we change variables. Following the same procedure as described in the notes on Pressure (http://imechanica.org/node/885), we can define the enthalpy as

$$H(U,p,N) = U + pV,$$

the Helmholtz free energy as

$$F(T,V,N) = U - TS,$$

and the Gibbs free energy as

$$G(T,p,N) = U + pV - TS.$$

These functions are used to interpret experiments with alternative sets of independent variables.

The chemical potential can be defined in many alternative, but equivalent, ways:

$$\mu = \frac{\partial U(S,V,N)}{\partial N} = \frac{\partial H(S,p,N)}{\partial N} = \frac{\partial F(T,V,N)}{\partial N} = \frac{\partial G(T,p,N)}{\partial N}.$$

For example, the definition

$$\mu = \frac{\partial F(T,V,N)}{\partial N}$$

may be easier to use than other definitions. It says the chemical potential of a species of molecules in a system is the change in the Helmholtz free energy of the system associated with adding one molecule of the species to the system, while maintaining *T* and *V* constant. Maintaining constant temperature may be easier than maintaining constant entropy. We can readily confirm that

$$\delta F = -S\delta T - p\delta V + \mu\delta N.$$

We can also state the corresponding minimal principles for systems with internal variables. For example, for a system characterized by three independent variables (T, V, N) and an internal variable *Y*, the Helmholtz free energy is a function of the four variables,

$$F = F(T, V, N, Y).$$

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

Exercise. Note that the chemical potential of a species of molecules in a pure substance coincides with the Gibbs free energy per molecule:

$$\mu = u - Ts + pv.$$

Derive this result from an alternative definition of the chemical potential:

$$\mu = \frac{\partial G(T, p, N)}{\partial N}.$$

Can you see what makes the Gibbs free energy special?

Chemical potential as an independent variable. We can also make the chemical potential as an independent variable. Recall the expression

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

and the interpretations of the partial derivatives:

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

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

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

If the function $S(U, V, N)$ is convex, the above equations can be inverted to express (U, V, N) in terms of (T, p, μ).

Define a function

$$\Lambda = U - TS + pV - \mu N.$$

Once we express (U, V, N) in terms of (T, p, μ), Λ is a function of (T, p, μ).

A combination of the above equations gives that

$$\delta\Lambda = -S\delta T + V\delta p - N\delta\mu.$$

The coefficients in the differential form can be defined by the partial derivatives of the function $\Lambda(T, p, \mu)$.