

Open system

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Part of my book on [Thermodynamics](#)

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Act Three: Entropy meets the number of molecules of one species in open systems, producing a child—chemical potential.

Given their analogous roles, why are we familiar with temperature, but not chemical potential?

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A family of isolated systems of many independent variables

Now enters another supporting actor—matter, represented by the number of molecules in every species. In thermodynamics, the number of a species of molecules, energy, and volume play analogous supporting roles, of equal importance.

An open system and its surroundings transfer energy, volume, and matter. The open system may contain many species of molecules. To illustrate ideas, assume that only two species—called species 1 and species 2—can transfer between the open system and

surroundings. The open system may contain molecules other than species 1 and 2. We assume that these other species do not transfer between the open system and the surroundings. The system and its surroundings are said to be separated by a *semipermeable wall*.

For an open system, let the energy be U , volume be V , the number of molecules of species 1 be N_1 , and the number of molecules of species 2 be N_2 . When U , V , N_1 , N_2 are fixed, the open system becomes an [isolated system](#). Denote the number of quantum states of this isolated system by $\Omega(U, V, N_1, N_2)$.

Recall the definition of [entropy](#):

$$S(U, V, N_1, N_2) = k_B \log \Omega(U, V, N_1, N_2)$$

As U , V , N_1 , N_2 vary, the function $S(U, V, N_1, N_2)$ characterizes the open system as a *family of isolated systems*.

Definition of chemical potential

For the function of the four independent variables, $S(U, V, N_1, N_2)$, recall a fact of calculus:

$$\begin{aligned} dS &= (\partial S(U, V, N_1, N_2) / \partial U) dU \\ &+ (\partial S(U, V, N_1, N_2) / \partial V) dV \\ &+ (\partial S(U, V, N_1, N_2) / \partial N_1) dN_1 \\ &+ (\partial S(U, V, N_1, N_2) / \partial N_2) dN_2 \end{aligned}$$

Between the open system and its surroundings, when we block the transfer of molecules, but allow the transfer of energy and volume, the open system becomes a [closed system](#). We have already related two partial derivatives to thermodynamic properties:

$$\begin{aligned} 1/T &= \partial S(U, V, N_1, N_2) / \partial U \\ P/T &= \partial S(U, V, N_1, N_2) / \partial V \end{aligned}$$

The other two partial derivatives define the *chemical potentials*:

$$\begin{aligned} -\mu_1/T &= \partial S(U, V, N_1, N_2) / \partial N_1 \\ -\mu_2/T &= \partial S(U, V, N_1, N_2) / \partial N_2 \end{aligned}$$

The ratio μ_1/T is the child of the union of the entropy and the number of molecules of species 1. The ratio μ_2/T is the child of the union of the entropy and the number of molecules of species 2. The chemical potentials are intensive thermodynamic properties.

The unit for a chemical potential is energy per molecule. Often, the amount of molecules is measured in moles, so that the unit for a chemical potential is energy per mole. Occasionally, a

chemical potential is reported in the unit of energy per unit mass. So, watch out for the unit used for a chemical potential.

Write

$$dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$$

This equation applies to an open system, and generalizes the equation for a thermal system, and the equation for a closed system.

For an open system, temperature measures the tendency of energy escaping from the open system, pressure measures the tendency of volume adding to the open system, and chemical potential of a molecular species measures the tendency of the species escaping from the open system.

Caution. Nature presents us with derivatives like $\partial S(U,V,N_1,N_2)/\partial N_1$. Humans like to name them. The names, of course, make no difference to any phenomena. This irrational definition of chemical potential, $-\mu_1/T = \partial S(U,V,N_1,N_2)/\partial N_1$, comes to us from Gibbs (1875). A more rational practice would name $\partial S(U,V,N_1,N_2)/\partial N_1$ directly! It would be a dimensionless number and simple to understand.

Two open systems in contact

Two open systems, A and B, are said to be in contact if they transfer energy, space, and matter. We next analyze the two open systems in contact using the [basic algorithm of thermodynamics](#).

Step 1. Construct an isolated system with internal variables. Characterize system A by a function $S_A(U_A, V_A, N_{1,A}, N_{2,A})$, and system B by another function $S_B(U_B, V_B, N_{1,B}, N_{2,B})$. We have to introduce a few quantities of two subscripts; for example, $N_{1,A}$ denotes the number of molecules of species 1 in system A. We make the composite of the two open systems into an isolated system. The isolated system conserves energy, space, and matter:

$$U_A + U_B = \text{constant}$$

$$V_A + V_B = \text{constant}$$

$$N_{1,A} + N_{1,B} = \text{constant}$$

$$N_{2,A} + N_{2,B} = \text{constant}$$

Here the conservation of matter means the following. We assume that the two species of molecules do not undergo a chemical reaction, so that the number of molecules in each species is conserved. The composite is an isolated system of four independent internal variables: U_A , V_A , $N_{1,A}$, $N_{2,A}$. Note that

$$dU_A + dU_B = 0$$

$$dV_A + dV_B = 0$$

$$dN_{1,A} + dN_{1,B} = 0$$

$$dN_{2,A} + dN_{2,B} = 0$$

Step 2. Find the subset entropy of the isolated system as a function of the internal variables. When the independent internal variables $U_A, V_A, N_{1,A}, N_{2,A}$ are fixed at particular values, the isolated system flips in a subset of the sample space. Denote the subset entropy by $S_{\text{composite}}(U_A, V_A, N_{1,A}, N_{2,A})$. Entropy is an extensive quantity, so that the subset entropy is a sum:

$$S_{\text{composite}}(U_A, V_A, N_{1,A}, N_{2,A}) = S_A(U_A, V_A, N_{1,A}, N_{2,A}) + S_B(U_B, V_B, N_{1,B}, N_{2,B})$$

When the internal variables change by $dU_A, dV_A, dN_{1,A}, dN_{1,B}$, the subset entropy of the isolated system changes by

$$dS_{\text{composite}} = (1/T_A - 1/T_B)dU_A + (P_A/T_A - P_B/T_B)dV_A + (-\mu_{1,A}/T_A + \mu_{1,B}/T_B)dN_{1,A} + (-\mu_{2,A}/T_A + \mu_{2,B}/T_B)dN_{2,A}$$

Step 3. Change the internal variables to maximize the subset entropy for the isolated system to equilibrate. The four internal variables $U_A, V_A, N_{1,A}, N_{2,A}$ can change independently. When the isolated system equilibrates, the subset entropy maximizes, $dS_{\text{composite}} = 0$, so that

$$T_A = T_B$$

$$P_A = P_B$$

$$\mu_{1,A} = \mu_{1,B}$$

$$\mu_{2,A} = \mu_{2,B}$$

Equilibrium requires four conditions. The two open systems have the equal temperature, equal pressure, equal chemical potential of molecular species 1, and equal chemical potential of molecular species 2. Like temperature and pressure, the chemical potential of each species of molecules is an intensive property.

Step 4. Change the internal variables to increase the subset entropy for the isolated system to undergo an irreversible process. Out of equilibrium, the algorithm requires that the subset entropy should increase as time progresses, $dS_{\text{composite}} > 0$.

Consider a situation where the two open systems are in partial equilibrium, $T_A = T_B$, $P_A = P_B$, $\mu_{1,A} = \mu_{1,B}$, but not in equilibrium with respect to the transfer of molecular species 2. The inequality $dS_{\text{composite}} > 0$ reduces to

$$(-\mu_{2,A} + \mu_{2,B})dN_{2,A} > 0$$

Thus, molecular species 2 transfers from the system of high chemical potential to the system of low chemical potential. The presence of the negative sign in the definition of chemical potential leads to this verbal convenience. The chemical potential of a molecular species in an open system measures the tendency of the species to escape from the open system.

The basic algorithm keeps track of energy, volume, and matter, and never needs the hair-splitting definition of heat and work. Indeed, defining heat and work for an open system is more convoluted than that for a closed system. We will never need such a convoluted notion.

Pure substance

Consider the chemical potential of a species of molecules in a pure substance.

Chemical potential is a function of temperature and pressure, $\mu(T,P)$. We model a piece of a pure substance as an open system of a characteristic function $S(U,V,N)$. Write

$$dS = (1/T)dU + (P/T)dV - (\mu/T)dN$$

We can increase the number of molecules in the piece without changing the functions of state per molecule, u , v , s , and without changing T , P , μ . When we add dN number of molecules to the piece, the extensive functions of state change by

$$dS = sdN$$

$$dU = udN$$

$$dV = vdN$$

The equation $dS = (1/T)dU + (P/T)dV - (\mu/T)dN$ becomes

$$s = (1/T)u + (P/T)v - (\mu/T)$$

Rearranging, we find that

$$\mu = u + Pv - Ts$$

By this equation alone, it is not obvious that the chemical potential is a function of T and P . Recall that in an equilibrium mixture of two or three homogeneous states, the intensive variables T and P are the same in every homogeneous state, each of the extensive variables u , v , s takes a different value in each homogeneous state.

When a state water and a state of steam equilibrate, the chemical potential of H_2O molecules in the two states are the same:

$$\mu_{\text{water}} = \mu_{\text{steam}}$$

When a state of water, a state of ice, and a state of steam equilibrate, the chemical potential of H_2O molecules in the three states are the same:

$$\mu_{\text{water}} = \mu_{\text{ice}} = \mu_{\text{steam}}$$

Consequently, the chemical potential of a species of molecules in a pure substance is a function of two variables, $\mu(T,P)$.

Derivatives of the function $\mu(T,P)$. Recall that

$$ds = (1/T)du + (P/T)dv$$

$$\mu = u + Pv - Ts$$

A combination of the two equations gives that

$$d\mu = -sdT + vdP$$

This equation suggests that

$$\partial\mu(T,P)/\partial T = -s$$

$$\partial\mu(T,P)/\partial P = v$$

The function $\mu(T,P)$ is smooth when the pure substance equilibrates in a homogeneous state, but changes slopes abruptly when the substance undergoes a phase transition.

Determine chemical potential of H_2O by steam tables

Look again at the chemical potential of a species of molecules in pure substance:

$$\mu = u + Pv - Ts$$

Of the five quantities on the right-hand side of the equation, only energy u has an arbitrary additive constant. The same additive constant appears in the chemical potential of the molecular species in the pure substance. As we have recognized in the chapter on [chemical reaction](#), the “arbitrary additive constant” cannot be totally arbitrary.

Recall the definition of [enthalpy](#): $h = u + Pv$. Write the equation $\mu = u + Pv - Ts$ as

$$\mu = h - Ts$$

The chemical potential of H_2O in pure H_2O is a function of temperature T and pressure P . The function is determined using enthalpy and entropy listed in steam tables.

On a whim of an international committee, steam tables set enthalpy and entropy to be zero for a state of water. This convention is inappropriate when chemical potential is used in chemical reactions. Rather, we should update the enthalpy of water according to the [enthalpy of formation](#), and update the entropy to [absolute entropy](#).

Experimental determination of the chemical potential of a species of molecules in any open system

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

Now let us measure the chemical potential of H_2O in an arbitrary open system, such as a bottle of wine. We can bring the bottle of wine into contact with a flask of pure water vapor. The contact is made with a semipermeable membrane that allows H_2O molecules to go through, but blocks all other species of molecules. When the wine in the bottle equilibrates with the vapor in the flask, the two systems have the same temperature and the same chemical potential of H_2O . A reading of the temperature and pressure in the flask determines the chemical potential of H_2O in the flask, which is the same as the chemical potential of H_2O in the wine.

In summary, we measure the chemical potential of a species of molecules in any system as follows.

1. Find the chemical potential of the species of molecules in pure substance as a function of temperature and pressure, $\mu(T,P)$.
2. Use a semipermeable wall to equilibrate the system and the pure substance.
3. Read the temperature and pressure in the pure substance.

Once the principle is established, one can invent convenient methods to measure chemical potentials. The development of chemical sensing parallels that of thermometry.

Electronic nose

Humans smell alcohol but not water. Dogs may have a better sense of smell than humans for many species of molecules. An active field of research is to develop electronic noses to detect trace amounts of molecules in the air.

Given an open system, every species of molecules in the system will release a vapor into the surrounding air. We can determine the chemical potential of every species in the air, which equals the chemical potential of the species in the open system. That is, the electronic nose can smell the content of the open system.

Temperature vs. chemical potential

Usage of words. When speaking of a chemical potential, we should identify both the molecular species and the open system. For example, we speak of the chemical potential of water molecules in a piece of cheese, or the chemical potential of water molecules in a glass of wine. We also speak of the chemical potential of carbon dioxide in a bottle of Coca Cola. Denote the chemical potential of molecular species 1 in open system A by $\mu_{1,A}$.

When we speak of temperature, we only need to identify the place. For example, we speak of the temperature of a piece of cheese, or the temperature of a glass of wine.

This difference in usage comes from something fundamental: our world has many species of molecules, but only one species of energy. For the time being, we consider processes in which the number of each species of molecules is conserved; for example, the number of oxygen molecules is conserved, and the number of nitrogen molecules is conserved. By contrast, all forms of energy can convert to one another: it is the total energy that is conserved.

Experimental significance of temperature. The temperature of a system measures the change in the entropy of the system associated with the change in energy. Energy flows from a place of high temperature to a place of low temperature. Temperature corresponds to the daily experience of hotness. Indeed, our daily experience of hotness is so pervasive that it may even impede our learning of thermodynamics. It takes significant effort for us to sort out, of all our feelings for hotness, what is essential and what is incidental. Only then we can link our daily experience of hotness to the thermodynamics of temperature.

Experimental significance of a chemical potential. The chemical potential of ethanol in a glass of wine measures the escaping tendency of ethanol from the wine. Ethanol goes from a place of high chemical potential to a place of low chemical potential. Chemical potential corresponds to the daily experience of the smell of the wine.

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

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

Why are we familiar with temperature, but not chemical potential?

Given similarly pervasive roles of temperature and chemical potential in nature, we may wonder why we do not have the same level of familiarity with the two quantities.

I can think of two reasons: cultural and technical.

Blame our parents. 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 in the wine is high. The phrase—the chemical potential of ethanol in the wine—is simply not in the everyday language. So blame our parents.

Blame our world. 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. The world confuses us with too many species of molecules! So blame our world.

No litter

Littered in literature are quantities directly related to chemical potentials. Examples include [fugacity](#), [activity](#), [water potential](#), and [affinity](#). They add no value, and should never exist. If you have to read papers that contain these quantities, look up their definitions in Wikipedia, and convert them back to chemical potentials.

Unfinished business of collecting big data

Steam tables took centuries to construct. That is for a single pure substance, H_2O molecules. The task becomes even more onerous for a system made of more species of molecules. Despite persistent attempts since Gibbs (1875) cast thermodynamics in the present form, the problem of collecting data for practical systems remains an unfinished business. Experimentals are increasingly augmented by computations. Applied thermodynamics is an active field of research.

Incompressible pure substance

In many applications of liquids and solids, the pressure is small, so that the volume per molecule in the system v , is taken to be independent of the pressure, and the system is called *incompressible*.

Recall the chemical potential of a species of molecules in a pure substance:

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

For an incompressible substance, u , v , and s are functions of T , and are independent of P . Let P_0 be a reference pressure. Write

$$\mu(T,P) = \mu(T,P_0) + (P - P_0)v(T).$$

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

Pure ideal gas

An ideal gas, of N molecules of a single species in a flask of volume V , is subject to pressure P and temperature T . Recall the equations of states:

$$\begin{aligned} PV &= Nk_B T \\ dU &= Nc_V(T)dT \\ dH &= Nc_P(T)dT, \quad c_P(T) = c_V(T) + k_B \\ dS &= (Nc_P(T)/T)dT - (Nk_B/P)dP \end{aligned}$$

Also write these equations as

$$\begin{aligned} PV &= Nk_B T \\ U &= Nu(T) \\ H &= Nh(T), \quad h(T) = u(T) + k_B T \\ S &= Ns(T, P), \quad s(T, P) = s(T, P_0) - k_B \log(P/P_0) \end{aligned}$$

Here P_0 is a reference pressure. The two functions, $h(T)$ and $s(T, P_0)$, are listed in the ideal gas tables for various species of molecules.

The chemical potential $\mu = u + Pv - Ts$ can be written as

$$\mu(T,P) = h(T) - Ts(T,P_0) + k_B T \log(P/P_0)$$

Ideal gas mixture

The chemical potential of molecules of species 1 in an ideal gas mixture is

$$\mu_1(T,P_1) = h_1(T) - Ts_1(T,P_0) + k_B T \log(P_1/P_0)$$

Here P_1 is the partial pressure of species 1 in the mixture. The functions $h_1(T)$ and $s_1(T, P_0)$ are the same as those of a pure ideal gas, and are available for many species of molecules. Thus, to determine the chemical potential of a species of molecules in an ideal gas mixture, we just measure the partial pressure of the species in the mixture.

Relative humidity

At a given temperature, when moist air is in equilibrium with liquid water, we say that the air is saturated with water. If air contains fewer water molecules than the saturated air does, the number of water molecules in the air divided by the number of water molecules in the saturated air is called the relative humidity. Write

$$RH = N/N_{\text{sat}}$$

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

$$RH = P/P_{\text{sat}}$$

where P is the partial pressure of H_2O in the unsaturated gas, $P < P_{\text{sat}}$

Write the chemical potential of water in the air as

$$\mu(T, P) = \mu(T, P_{\text{sat}}) + k_B T \log(P/P_{\text{sat}})$$

The chemical potential of H_2O in moist air relates to the relative humidity. Our parents are not totally negligent. They do mention humidity.

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

Gibbs function

We can derive numerous mathematical relations involving chemical potentials. These mathematical relations are inessential for the understanding of thermodynamics, but may bring convenience in applications. I will not spend much time on such relations, but will give a few examples.

Recall the definition of the [Gibbs function](#):

$$G = U - TS + PV$$

Energy U is a relative property, and T , S , P , and V are absolute properties. The same additive constant appears in U also appears in the Gibbs function.

Recall

$$dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$$

A combination of the above two equations gives that

$$dG = -SdT + VdP + \mu_1dN_1 + \mu_2dN_2$$

This equation suggests that the Gibbs function be regarded as a function $G(T, P, N_1, N_2)$, with the partial derivatives

$$-S = \partial G(T, P, N_1, N_2) / \partial T$$

$$V = \partial G(T, P, N_1, N_2) / \partial P$$

$$\mu_1 = \partial G(T, P, N_1, N_2) / \partial N_1$$

$$\mu_2 = \partial G(T, P, N_1, N_2) / \partial N_2$$

Once the Gibbs function $G(T, P, N_1, N_2)$ is known, the above equations calculate the other functions: $S(T, P, N_1, N_2)$, $V(T, P, N_1, N_2)$, $\mu_1(T, P, N_1, N_2)$, $\mu_2(T, P, N_1, N_2)$.

Binary system

Up to this point, the open system is made of many species of molecules, and only two species molecules, 1 and 2, can exchange between the open system and the surroundings. We next consider a special case, where the open system is made of two species of molecules, and both can exchange with the surroundings. Such an open system is called a *binary system*.

A state of a binary system is specified by three independent intensive properties. In an open system made of two species of molecules, let the numbers of molecules of the two species be N_1 and N_2 , and the number fraction of species 1 be

$$y_1 = N_1 / (N_1 + N_2)$$

A state of the system is specified by the values of three properties: T , P , and y_1 .

The chemical potential of species 1 in the open system is an intensive property, and should be a function of the three independent intensive properties, $\mu_1(T, P, y_1)$. Similarly, the chemical potential of species 2 in the open system is a function of the three independent intensive properties, $\mu_2(T, P, y_1)$.

Gibbs function per molecule. The Gibbs function is an extensive property. Define the Gibbs function per molecule by

$$g = G/(N_1 + N_2)$$

Similarly define energy per molecule, u , volume per molecule, v , and entropy per molecule s .

The Gibbs function per molecule is a function of three variables, $g(T, P, y_1)$. We can use $g(T, P, y_1)$ to express other function of states. Recall that

$$\begin{aligned} g &= u + Pv - Ts \\ -s &= \partial g(T, P, y_1) / \partial T \\ v &= \partial g(T, P, y_1) / \partial P \end{aligned}$$

We can also use $g(T, P, y_1)$ to express $\mu_1(T, P, y_1)$ and $\mu_2(T, P, y_1)$.

$$\begin{aligned} \mu_1(T, P, y_1) &= \partial G(T, P, N_1, N_2) / \partial N_1 \\ &= \partial((N_1 + N_2)g(T, P, y_1)) / \partial N_1 = g(T, P, y_1) + (N_1 + N_2) \partial g(T, P, y_1) / \partial N_1 \\ &= g(T, P, y_1) + (N_1 + N_2) (\partial g(T, P, y_1) / \partial y_1) (\partial y_1 / \partial N_1) \\ &= g(T, P, y_1) + (N_1 + N_2) (\partial g(T, P, y_1) / \partial y_1) (1 / (N_1 + N_2) - N_1 / (N_1 + N_2)^2) \\ &= g(T, P, y_1) + (1 - y_1) (\partial g(T, P, y_1) / \partial y_1) \end{aligned}$$

Thus,

$$\mu_1(T, P, y_1) = g(T, P, y_1) + (1 - y_1) (\partial g(T, P, y_1) / \partial y_1)$$

Similarly,

$$\mu_2(T, P, y_1) = g(T, P, y_1) - y_1 \partial g(T, P, y_1) / \partial y_1$$

Thus, $g(T, P, y_1)$ is a characteristic function of an open system made of two species of molecules.

Exercise. Confirm the expression for $\mu_2(T, P, y_1)$.

Exercise. For fixed T and P , interpret $\mu_1(T, P, y_1)$ and $\mu_2(T, P, y_1)$ graphically on the g - y_1 plane.

Exercise. Define the Helmholtz function by $F = U - TS$. Show that $\mu_1 = \partial F(T, V, N_1, N_2) / \partial N_1$.

Exercise. An open system of three species molecules is characterized by four independent intensive properties. Express the chemical potential of one species in the open system in terms of the Gibbs function per molecule.

Homogeneous function

Homogeneous function in calculus. Let $Z(X,Y)$ be a function. The results below readily generalize to a function of any number of independent variables. Denote $a = \partial Z(X,Y)/\partial X$ and $b = \partial Z(X,Y)/\partial Y$. Recall a fact of calculus: $dZ = a dX + b dY$.

A function $Z(X,Y)$ is called a *homogeneous function* if, for any number λ , the following relation holds:

$$\lambda Z(X,Y) = Z(\lambda X, \lambda Y)$$

Euler relation. For a homogeneous function, $Z(X,Y)$, when X , Y and Z are multiplied by a number λ , the two slopes, a and b , do not change. Thus, we can write $dZ = a dX + b dY$ as $d(\lambda Z) = a d(\lambda X) + b d(\lambda Y)$. Recall that $d(\lambda Z) = Z d\lambda + \lambda dZ$, $d(\lambda X) = X d\lambda + \lambda dX$, and $d(\lambda Y) = Y d\lambda + \lambda dY$. The equation $d(\lambda Z) = a d(\lambda X) + b d(\lambda Y)$ becomes that

$$Z = aX + bY$$

This equation is called the *Euler relation*.

Gibbs-Duhem relation. Taking derivative of the Euler equation, we obtain that $dZ = a dX + X da + b dY + Y db$. This equation, along with $dZ = a dX + b dY$, gives that

$$X da + Y db = 0$$

This equation is called the *Gibbs-Duhem relation*.

Homogeneous function in thermodynamics. We next apply these facts of calculus to a binary system, characterized by the function $S(U,V,N_1,N_2)$. Recall that

$$dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$$

This equation identifies the four partial derivatives of the function $S(U,V,N_1,N_2)$. The function $S(U,V,N_1,N_2)$ involves five extensive properties, and is a homogeneous function. The four partial derivatives of the function define the four intensive properties. When we multiply every extensive property by a number λ , the open system increases size proportionally, but all the intensive properties remain unchanged.

The Euler relation for the homogeneous function $S(U,V,N_1,N_2)$ is

$$S = U/T + PV/T - N_1\mu_1/T - N_2\mu_2/T$$

This equation, along with the definition of the Gibbs function, $G = U - TS + PV$, gives an identity:

$$G = \mu_1 N_1 + \mu_2 N_2$$

For the open system, invert the function $S(U, V, N_1, N_2)$ to obtain the function $U(S, V, N_1, N_2)$, which is also a homogeneous function. From $dS = (1/T)dU + (P/T)dV - (\mu_1/T)dN_1 - (\mu_2/T)dN_2$ we obtain that

$$dU = TdS - PdV + \mu_1 dN_1 + \mu_2 dN_2$$

This equation identifies the four partial derivatives of the function $U(S, V, N_1, N_2)$. The Gibbs-Duhem relation for the function $U(S, V, N_1, N_2)$ is

$$SdT - VdP + N_1 d\mu_1 + N_2 d\mu_2 = 0$$