ADVANCED THERMODYNAMICS

Handout II – Auxiliary Functions, Statistical Thermodynamics, the Third Law and the Enthalpy Balance

(Gaskell Chapters 4- 6)

BACKGROUND

This handout essentially follows Gaskell’s book, but in a different order and with supplementary material. Auxiliary functions is considered first, as this subject follows the combined FL and SL naturally and does not require statistical thermodynamics. As is the case historically, statistical thermodynamics (ST) follows the development of the Kinetic Theory of gases (KTG, see HI) and is essential to understanding the Third Law of Thermodynamics (TL). Finally with these underpinnings, the important parameter of heat capacity can be better understood. The handout ends with application of the heat capacity in the enthalpy balance of chemical reactions and other processes.

AUXILIARY FUNCTIONS

The need for the co-called auxiliary functions is due simply to the fact that the dependent variables defining various criteria for equilibrium are not convenient ones from the point of view of experimentation. For example, ***T***, ***P*** and ***V*** are much easier to control in an experiment than, say, ***S*** or ***U***! Auxiliary functions provide the apparatus for converting inconvenient dependent variables into independent ones. Also, there is a need to consider work other than that of expansion of a gas against external pressure, such as chemical work in the various criteria for equilibrium, as composition plays a key role in establishing the equilibrium state for the materials system.

Two New State Functions: the Helmholtz and Gibbs Free Energy Functions

In the previous handout, it was shown that the sum of the entropy change of a system and its surroundings is zero for a reversible process, and is greater than zero for a spontaneous process.

It is not convenient to calculate, or experimentally measure, entropy change for either the system or the surroundings in many cases. So, it is desirable to find some other function of state variables *for the system alone* which would indicate whether or not a given process is potentially spontaneous. Such a function is called the Free Energy Function, of which there are two, depending on the independent variables:

The Helmholtz Free Energy:

$$\boldsymbol{A \equiv U - TS}$$

The Gibbs Free Energy:

$$\boldsymbol{G \equiv H - TS}$$

Starting with the FL, a review is in order (See HI):

$$\boldsymbol{dU = \delta q - \delta w}$$

But:

$$\boldsymbol{dS = \frac{\delta q}{T} + dS_{irr}} \Rightarrow$$

$$\boldsymbol{dU = TdS - TdS_{irr} - \delta w}$$

If $\boldsymbol{\delta w}$ is only volume work ($= \boldsymbol{PdV}$) then this equation becomes:

$$\boldsymbol{dU = TdS - TdS_{irr} - PdV}$$

If only *reversible* changes are considered:

$$\boxed{\boldsymbol{dU_{rev} = TdS - PdV}}$$

Similarly (since $\boldsymbol{H \equiv U + PV}$), $\boldsymbol{dH = TdS - TdS_{irr} + VdP} \Rightarrow$

$$\boxed{dH_{rev} = TdS + VdP}$$

Including dS_{irr}, these two equations were already shown to be a criteria for spontaneous processes; viz.:

$$\boxed{dU_{S,V} = -TdS_{irr} \leq 0}$$

And

$$\boxed{dH_{S,P} = -TdS_{irr} \leq 0}$$

But, as stated earlier, measuring or calculating dS_{irr} is not easy, as it is not naturally subjected to external control.

We can re-arrange the equation for U as:

$$\delta w = TdS - dU - TdS_{irr}$$

And, since dS_{irr} cannot be negative, we get:

$$\delta w \leq TdS - dU$$

Integration of the above equation for constant T gives:

$$w \leq T(S_2 - S_1) - (U_2 - U_1)$$

Or

$$w \leq T\Delta S - \Delta U$$

This last expression represents the *maximum* work that can be performed by the system on its surroundings during a change in state at constant T. This maximum work is performed *only* for a reversible process (hence, the equality); if the process is irreversible, it is less efficient, with less work preformed (hence, the inequality). So, we get:

$$-[(U_2 - TS_2) - (U_1 - TS_1)]_T = \textbf{available work}$$

The quantity $A \equiv U - TS$ represents the portion of the internal energy of a system that is free to do work without lowering the temperature.

The foregoing states that it is possible to devise a criterion for equilibrium that is dependent on the reversible change in entropy of the system, *not* on the change in irreversible entropy! our new criterion is:

$$-(A_2 - A_1) \geq w$$

Or

$$-dA_T \geq \delta w$$

For the simplest case of no volume work (i.e., constant volume) we have:

$$-dA_{T,V} \geq 0$$

Or

$$\boxed{dA_{T,V} \leq 0}$$

As before, the equality sign refers to reversible changes, and the inequality sign, to spontaneous changes.

That is to say that, during spontaneous changes in state at constant temperature and volume, the Helmholtz Free Energy of a system must decrease, and will continue to decrease until the system attains equilibrium, in which case, at equilibrium:

$$\boxed{dA_{T,V} = 0}$$

In contrast to the criterion that: $dS_{U,V} = 0\big|_{equil}$, now T and V are held constant instead of U and V, which is more practically realized.

Likewise, we can devise another criterion involving pressure as a dependent variable. Why is this so important? Because we live in a constant-pressure atmosphere, thus this condition is automatically fulfilled in many experimental situations!

We begin with defining work as volume work as well as other work $\boldsymbol{\delta w'}$:

$$\boldsymbol{\delta w = \delta w' + PdV}$$

We have from the criterion: $\boldsymbol{-dA_T \geq \delta w}$, so:

$$\boldsymbol{-dA_T \geq \delta w + PdV_T}$$

Or

$$\boldsymbol{dA_T + PdV_T \leq -\delta w'}$$

If the system is allowed to perform no work other than volume work ($\boldsymbol{PdV}$) then:

$$\boldsymbol{dA_{T,V} \leq 0}$$

This suggest a new criterion as a function of $\boldsymbol{dA_T}$ **and** $\boldsymbol{dV_T}$; viz.:

$$\boldsymbol{G \equiv H - TS = A + PV}$$

If we take the differential, we get:

$$\boldsymbol{dG = dA + PdV + VdP}$$

Then, we have:

$$\boxed{\boldsymbol{dG_{T,P} \leq -\delta w'}}$$

It is insightful to point out that the state property $\boldsymbol{G}$ bears the same relationship to the ability of the system to do work (other than volume work, or $\boldsymbol{w'}$) at constant $\boldsymbol{T}$ and $\boldsymbol{P}$ that

$\boldsymbol{A}$ bears to the ability of the system to do any work(*w'* as well as volume work) at constant $\boldsymbol{T}$.

If the system does *no* work other than volume work:

$$\boxed{dG_{T,P} \leq 0}$$

This means the Gibbs Free Energy of a closed system able to perform work on its surroundings can remain constant or decrease. (If isolated system, the work performed remains in the system.) Thus, at equilibrium:

$$\boxed{dG_{T,P} = 0}$$

To summarize, there are only three possibilities in the criteria for a change in state for a closed system:

1. **<0** – the process is possible and *will occur* (but at an undefined rate);
2. **>0** – the process is *not possible* and will not occur; or
3. **=0** – the initial and final states *co-exist in equilibrium*.

Given $\boldsymbol{A \equiv U - TS}$ and $\boldsymbol{G \equiv H - TS}$, we arrive at two more fundamental differential equations. As $\boldsymbol{A = U - TS \Rightarrow dA = dU - TdS - SdT}$, but $\boldsymbol{dU = TdS - PdV}$; therefore:

$$\boxed{dA = -SdT - PdV}$$

Similarly, as $\boldsymbol{= A + PV \Rightarrow dG = dA + PdV + VdP = -SdT - PdV + PdV + VdP}$, then:

$$\boxed{dG = SdT + VdP}$$

Following Gaskell, we can summarize a set of useful thermodynamic functions:

	$dU = TdS - PdV \; (-w'_{rev})$
$H = U + PV \Rightarrow$	$dH = TdS + VdP \; (-w'_{rev})$
$A = U - TS \Rightarrow$	$dA = -SdT - PdV \; (-w'_{rev})$
$G = H - TS \Rightarrow$	$dG = -SdT + VdP \; (-w'_{rev})$

Note that the variables on the RHS in the differential are independent variables, while those on the LHS are the dependent variables.

Combination of the various criteria for equilibrium given in HI involving ***S***, ***U*** and ***H*** with the two new criteria involving ***A*** and ***G***, we have the following summary in Table HII.1.

Table HII.1 - Thermodynamic Potentials, Conjugate (or Natural) Variables and the Criteria for Equilibrium.

State Property as a Thermodynamic Potential	Conjugate (or Natural) Variables	Criterion of Equilibrium
$S = S(U, V)$	***U, V***	$(dS_{U,V} \geq 0)$
$U = U(S, V)$	***S, V***	$(dU_{S,V} \leq 0)$
$H = H(S, P)$	***S, P***	$(dH_{S,P} \leq 0)$
$A = A(T, V)$	***T, V***	$(dA_{T,V} \leq 0)$
$G = G(T, P)$	***T, P***	$(dG_{T,P} \leq 0)$

Note in the above table the parallels of ***A*** and ***G*** (constant ***V*** versus constant ***P***, both at constant ***T***) and the fact that these two criteria involve convenient variables to be controlled in an experiment: ***T*** and ***V***, or ***T*** and ***P***.

Role of Composition and Size on Criterion For Equilibrium

Thus far, the discussion has been restricted to a closed system of fixed size and composition. In this case, these are only two independent variables, when fixed, completely fix the state of the system.

Obviously, if we let size and composition vary, we have more degrees of freedom and more than two independent variables:

- If composition is variable (in which the number of moles of various species change due to a chemical reaction) then minimization of $G_{T,P}$ only can occur at a unique composition (e.g., when a reaction equilibrium is established);
- As ***G*** is an extensive property (i.e., dependent on size of the system) the total number of moles must be specified to minimize $G_{T,P}$.

The Gibbs Free Energy, in addition to being a function of T and P, is also a function of the number of moles of all species present in the system:

$$G = G(T, P, n_i, n_j, n_k, \dots)$$

Complete differentiation of the above equation gives:

$$\boxed{dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,\dots} dP + \left(\frac{\partial G}{\delta n_i}\right)_{T,P,n_j,n_k} dn_i + \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_i,n_k,\dots} dn_j + \cdots}$$

If all moles remain constant: $dG \rightarrow -SdT + VdP$. On applying the rules of differentiation to $G = G(T, P)$, we get:

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,\dots} = -S$$

And

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,\dots} = V$$

The complete differential for dG can be stated more formally as:

$$\boxed{dG = -SdT + VdP + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,n_k} dn_i}$$

In this equation, there are k species, and the ith specie refers to the differentiation of G with respect to the number of moles of the ith species, holding all other species (n_j+$\dots$) constant.

The Chemical Potential

The following term is referred to as the chemical potential of species ***i***:

$$\boxed{\boldsymbol{\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,n_k}}}$$

The interpretation of $\boldsymbol{\mu_i}$ is the rate of increase of ***G*** when $\boldsymbol{n_i}$ moles of species *i* is added to the system at constant ***T*** and ***P*** and constant moles of all other species. Alternatively, if the system is sufficiently large, the addition of one mole of *i* at constant ***T*** and ***P*** does not measurably change the overall composition of the system, and thus $\boldsymbol{\mu_i}$ is the increase in ***G*** by this addition. So, we can state the complete differential of ***G*** as:

$$\boxed{\boldsymbol{dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dn_i}}$$

Note that $\boldsymbol{\mu_i}$ is defined with respect to *mass* ($\boldsymbol{n_i}$) not mole fraction ($\boldsymbol{x_i}$)! To restate $\boldsymbol{\mu_i}$ as a function of mole fraction involves a somewhat complicated maneuver that is discussed in HIII, as the resulting equation for $\boldsymbol{\mu_i}$ is employed in the computation of phase equilibria. Also it is noted that if the composition remains virtually constant as one mole of $\boldsymbol{n_i}$ is added, this means that the system is *open*. On the other hand, $\boldsymbol{n_i}$ can still vary in a closed system that may be undergoing a chemical reaction, where the total number of moles is constant, but the various moles of particular species change in accordance to the chemical reaction occurring.

We can now enlarge our set of differentials of thermodynamic potentials (where: $\boldsymbol{w'_{rev} = \sum_i^k \mu_i dn_i}$) to:

$$dU = TdS - PdV - \sum_i^k \mu_i dn_i$$
$$dH = TdS + VdP - \sum_i^k \mu_i dn_i$$
$$dA = SdT - PdV - \sum_i^k \mu_i dn_i$$
$$dG = SdT + VdP - \sum_i^k \mu_i dn_i$$

But, we can deduce that the *total differential* of each thermodynamic potential must include a term involving the rate of change of that potential with respect to changes in composition; viz.:

$$dU = TdS - PdV - \sum_i^k \left[\frac{\partial U}{\partial n_i}\right]_{S,V,n_j} dn_i$$
$$dH = TdS + VdP - \sum_i^k \left[\frac{\partial H}{\partial n_i}\right]_{S,P,n_j} dn_i$$
$$dA = SdT - PdV - \sum_i^k \left[\frac{\partial A}{\partial n_i}\right]_{T,V,n_j} dn_i$$
$$dG = SdT + VdP - \sum_i^k \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_j} dn_i$$

So, we have the following identity that must be true:

$$\left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_j} = \mu_i = \left[\frac{\partial U}{\partial n_i}\right]_{S,V,n_j} = \left[\frac{\partial H}{\partial n_i}\right]_{S,P,n_j} = \left[\frac{\partial A}{\partial n_i}\right]_{T,V,n_j}$$

This means that we have three equivalent definitions for μ_i! Thus, we can re-state our list of equations for the total differential of the four fundamental thermodynamic potentials, where it is seen we have another conjugate variable, n_i:

$\boldsymbol{U = U(S, V, n_i) \Rightarrow}$	$\boldsymbol{dU = TdS - PdV + \sum_i^k \mu_i dn_i}$
$\boldsymbol{H = H(S, P, n_i) \Rightarrow}$	$\boldsymbol{dH = TdS + VdP + \sum_i^k \mu_i dn_i}$
$\boldsymbol{A = A(T, V, n_i) \Rightarrow}$	$\boldsymbol{dA = -SdT - PdV + \sum_i^k \mu_i dn_i}$
$\boldsymbol{G = G(T, P, n_i) \Rightarrow}$	$\boldsymbol{dG = -SdT + VdP + \sum_i^k \mu_i dn_i}$

To recap, the FL is:

$$\boldsymbol{dU = \delta q - \delta w}$$

For a closed system undergoing a reversible change in composition (such as due to a reversible chemical reaction):

$\boldsymbol{\delta q = TdS}$, then:

$$\boldsymbol{\delta w = PdV + \sum_i^k \mu_i \, dn_i}$$

Clearly the term

$$\boldsymbol{\sum_i^k \mu_i \, dn_i}$$

is the chemical work done by the system (denoted as $\boldsymbol{w'}$) which is in addition to the volume work $\boldsymbol{PdV}$.

Thermodynamic Relations and the Maxwell Equations

As stated earlier, it is of supreme importance to be able to manipulate thermodynamic variables for experimental or computational convenience. Because the four key thermodynamic potentials are state properties, and because only three (independent) variables need to be defined to completely define the state of the open system (only two independent variables are needed for a closed system), we can write the total differential, and then deduce the total differential just given for these four thermodynamic potentials:

$U = U(S,V,n_i) \Rightarrow$	$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial n_i}\right)_{S,V} dn_i \Rightarrow$	$\left(\frac{\delta U}{\delta S}\right)_V = T$	$\left(\frac{\delta U}{\delta V}\right)_S = -P$
$H = H(S,P,n_i) \Rightarrow$	$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP + \left(\frac{\partial H}{\partial n_i}\right)_{S,P} dn_i \Rightarrow$	$\left(\frac{\delta H}{\delta S}\right)_P = T$	$\left(\frac{\delta H}{\delta P}\right)_S = V$
$A = A(T,V,n_i) \Rightarrow$	$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial n_i}\right)_{V,T} dn_i \Rightarrow$	$\left(\frac{\delta A}{\delta T}\right)_V = -S$	$\left(\frac{\delta A}{\delta V}\right)_T = -P$
$G = G(T,P,n_i) \Rightarrow$	$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P} dn_i \Rightarrow$	$\left(\frac{\delta G}{\delta T}\right)_P = -S$	$\left(\frac{\delta G}{\delta P}\right)_T = V$

From these results, we can deduce the following identities:

$T =$	$\left(\frac{\partial U}{\partial S}\right)_V$	$\left(\frac{\partial H}{\partial S}\right)_P$
$P =$	$-\left(\frac{\partial U}{\partial V}\right)_S$	$-\left(\frac{\partial A}{\partial V}\right)_T$
$V =$	$\left(\frac{\partial H}{\partial P}\right)_S$	$\left(\frac{\partial G}{\partial P}\right)_T$
$S =$	$-\left(\frac{\partial A}{\partial T}\right)_V$	$-\left(\frac{\partial G}{\partial T}\right)_P$

As reviewed in HI, state function $z = z(x,y)$, such that $\partial z = L(x,y)dx + M(x,y)dy$ is considered a perfect differential if:

$$\left(\frac{\partial L}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$$

In the above equation: $L(x,y) = \left(\frac{\partial z}{\partial x}\right)_y$ and $M(x,y) = \left(\frac{\partial z}{\partial y}\right)_x$

Then, we have

$$\frac{\partial L}{\partial y} = \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial M}{\partial x}$$

The four thermodynamic potentials are the function: $\boldsymbol{z = z(x, y)}$. The following table (HII.2) gives the so-called Maxwell Equations based on these potentials being perfect differentials (here, with *n* constant).

Table HII.2 - The Maxwell Equations

Thermodynamic Potential *Z*	**Total Differential**	***L***	***x***	***M***	***y***	**Maxwell Equations**	**Name**
U	$dU = TdS - PdV$	T	S	$-P$	V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V}$	**Energy Maxwell Eqn.**
H	$dH = TdS + VdP$	T	S	V	P	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial P \partial S}$	**Enthalpy Maxwell Eqn.**
A	$dA = SdT - PdV$	$-S$	T	$-P$	V	$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial^2 A}{\partial V \partial T}$	**Helmholtz Maxwell Eqn.**
G	$dG = -SdT + VdP$	$-S$	T	V	P	$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial P \partial T}$	**Gibbs Maxwell Eqn.**

Since the partials of the Maxwell equations can be inverted, we have:

$\left(\frac{\partial V}{\partial T}\right)_S =$	$-\left(\frac{\partial S}{\partial P}\right)_V$
$\left(\frac{\partial P}{\partial T}\right)_S =$	$\left(\frac{\partial S}{\partial V}\right)_P$
$\left(\frac{\partial V}{\partial S}\right)_T =$	$\left(\frac{\partial T}{\partial P}\right)_V$
$\left(\frac{\partial P}{\partial S}\right)_T =$	$\left(\frac{\partial T}{\partial V}\right)_P$

The Born Square

This is a mnemonic device that works because of the symmetry among the thermodynamic potentials and their conjugate variables. This is given in Figure HII.1

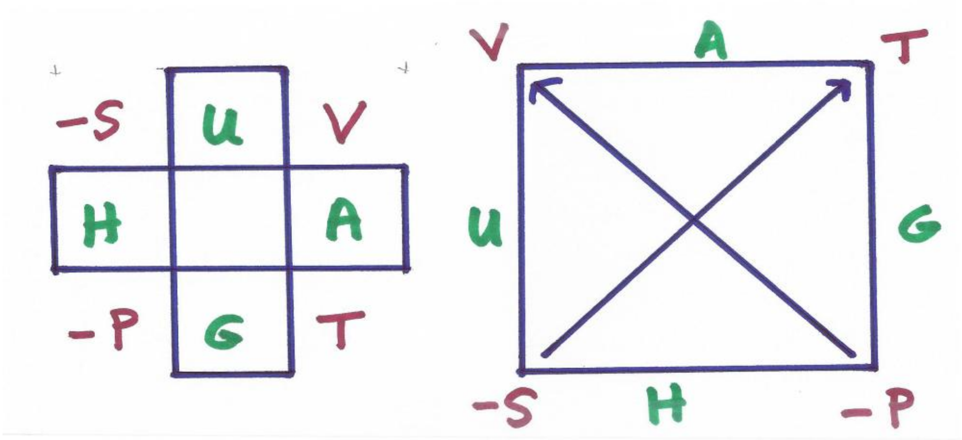


Figure HII.1-The Born Square showing the symmetrical relationship among the key thermodynamic potentials and their conjugate variables.

The Born Square works as follows. In the interior are four thermodynamic potentials (***U***, ***H***, ***A*** and **G**) that are flanked to each side by each potential's pair of conjugate variables. In turn, the two opposite corners of the square are the coefficients ***L*** and ***M*** of the exact differential of each potential. For example, taking ***U***, its conjugate pair are ***S*** and ***V***, and its exact differential are the coefficients L = ***T*** and M = ***-P*** for derivation of the Maxwell equation for ***U***. Crossing the square (the RHS of Figure HII.1) shows what differential to couple with the coefficient. For example, taking ***U***, ***P*** is paired with ***dV***, and ***T*** is paired with ***dS***, arriving at:

$$dU = TdS - PdV$$

Application of Maxwell’s Equations and Other Thermodynamic Relations

Measureable Properties

How does one measure the entropy or chemical potential from experiments? We can, typically, measure mechanical properties such as pressure; bulk quantities like volume and density; and thermal properties like temperature and heat flow.

Directly measureable thermodynamic variables are:

$$\boldsymbol{T}$$
$$\boldsymbol{P}$$
$$\boldsymbol{V}$$
$$\boldsymbol{N \text{ or } m}$$
$$\boldsymbol{\Delta H^{\alpha\to\beta}}$$

(*N* is the number of particles, and ***m*** is mass.)

Measureable materials properties that depend on derivatives of thermodynamic variables (due to a response to a perturbation) are called *response functions*. Several important ones are:

$$C_P = \left(\frac{\delta q_{rev}}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_V = \left(\frac{\delta q_{rev}}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Thermal compressibility at constant ***T***:

$$\boxed{\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}}$$

Coefficient of thermal expansion at constant ***P***:

$$\boxed{\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n} = \left(\frac{\partial \ln V}{\partial T}\right)_{P,n}}$$

Joule-Thomson coefficient:

$$\boxed{\boldsymbol{\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H}}$$

A great deal of effort by thermodynamic workers has been put into manipulation of the fundamental thermodynamic equations to change out dependent with independent variables and to position the dependent variables to be a function of directly measureable variables and one or more of the response functions. These manipulations almost always employ one or more of Maxwell's Equations and related identities, and often employ properties of exact differentials conferred by calculus (see HI). While a bit tricky, this procedure essentially follows these steps (which are somewhat arbitrary):

1. If the state function is a thermodynamic potential, start with its fundamental potential (this step can also be done as part of Step 6).

2. Construct a state function involving the variables of interest; if the state function is a thermodynamic potential, the variables of interest need not be conjugate variables, but ultimately, stem from conjugate pairs. Examples for an open system include: $\boldsymbol{H(T,P,N)}$, $\boldsymbol{S(T,P,N)}$, $\boldsymbol{\mu(V,P,N)}$ and $\boldsymbol{V(T,P,N)}$.

3. Write out the full total differential of the state function; e.g., for $\boldsymbol{P(T,P,V)}$:

$$\boldsymbol{dP = \left(\frac{\partial P}{\partial T}\right)_{V,N} dT + \left(\frac{\partial P}{\partial V}\right)_{T,N} dV + \left(\frac{\partial P}{\partial N}\right)_{V,T} dN}$$

4. Set to zero any differential that is constant; e.g., constant $\boldsymbol{N}$ for a closed system. Here it is important to remember any restrictions in further manipulations (in our example below, we must remember that $\boldsymbol{N}$ is being held constant):

$$\boldsymbol{dP = \left(\frac{\partial P}{\partial T}\right)_{V,N} dT + \left(\frac{\partial P}{\partial V}\right)_{T,N} dV}$$

5. Take the derivative of interest, essentially by dividing by the appropriate differential. We must specify any previously held constant conditions, as well as any additional constant conditions as is necessary to meet one less

than the number of independent variables. Continuing the same example above, we further specify that $\boldsymbol{S}$ is constant:

$$\left(\frac{\partial P}{\partial T}\right)_{S,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} dT + \left(\frac{\partial P}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial T}\right)_{S,N}$$

6. Substitute various fundamental equations (especially if the state function is a thermodynamic potential) to arrive at an expression of measureable quantities, including response variables and Maxwell equations.

In the above steps, the common techniques for manipulating partial differential equations from calculus are necessary (see HI).

Application of Maxwell Equations – Example 1

As an example, we here use one of Maxwell's equations and a response function. Consider:

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial^2 G}{\partial P \partial T}\right) = -\left(\frac{\partial V}{\partial T}\right)_P$$

But, we already know the coefficient of thermal expansion:

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Thus, we have:

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\alpha_P$$

Application of Maxwell Equations – Example 2

Here is a more complicated example for manipulation into response parameters; say, we want to know: $\left(\frac{\partial P}{\partial T}\right)_V = ?$

From Maxwell, we have:

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial^2 A}{\partial V \partial T}\right) = \left(\frac{\partial S}{\partial V}\right)_T$$

Now we want to use the property of partials:

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$$

So, we can re-arrange this equation to be:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} =$$

$$+\frac{V}{V}\frac{\alpha_P}{\beta_T} = \frac{\alpha_P}{\beta_T}$$

Application of Maxwell Equations – Example 3

Here we want to derive an equation for the change in entropy as a function of T and V for an ideal gas. Since S is a state variable, we immediately choose: $S = S(V, T)$, so, on differentiation, we get:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

We can replace $\partial S/\partial T$ with a function of c_V:

$$TdS = \delta q_V = dU = nc_V dT$$

Or

$$dS = \frac{nc_V dT}{T}$$

Or

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{nc_V}{T}$$

Similarly, we can replace $(\partial S/\partial V)_T$ with $(\partial P/\partial T)_V$ from Maxwell"s equations. So, we know have:

$$dS = \frac{nc_V dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$$

We know from the Ideal Gas Law;

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

So, we can substitute the above equation in to finally arrive at:

$$dS = \frac{nc_V dT}{T} + \frac{nR}{V} dV$$

It is noted that the above equation is readily integrated, giving:

$$\Delta S = S_2 - S_1 = nc_V \ln\frac{T_2}{T_1} + \mathrm{nR}\ln\frac{\mathrm{V_2}}{\mathrm{V_1}}$$

Application of Maxwell Equations – Example 4

As our final example, we will take two of the fundamental equations to arrive at functions that depend only on $\boldsymbol{T}$, $\boldsymbol{P}$ and $\boldsymbol{V}$ (closed system):

For internal energy, we have:

$$\boldsymbol{dU = TdS - PdV \Rightarrow}$$

$$\left(\frac{\partial \boldsymbol{U}}{\partial \boldsymbol{V}}\right)_{\boldsymbol{T}} = \boldsymbol{T}\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{V}}\right)_{\boldsymbol{T}} - \boldsymbol{P}$$

From Maxwell, we have:

$$\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{V}}\right)_{\boldsymbol{T}} = \left(\frac{\partial \boldsymbol{P}}{\partial \boldsymbol{T}}\right)_{\boldsymbol{V}}$$

So, we have:

$$\left(\frac{\partial \boldsymbol{U}}{\partial \boldsymbol{V}}\right)_{\boldsymbol{T}} = \boldsymbol{T}\left(\frac{\partial \boldsymbol{P}}{\partial \boldsymbol{T}}\right)_{\boldsymbol{V}} - \boldsymbol{P}$$

This result shows that the internal energy of a closed system is a function of measureable quantities $\boldsymbol{T}$, $\boldsymbol{V}$, and $\boldsymbol{P}$.

For enthalpy, we have:

$$\boldsymbol{dH = TdS + VdP \Rightarrow}$$

$$\left(\frac{\partial \boldsymbol{H}}{\partial \boldsymbol{P}}\right)_{\boldsymbol{T}} = \boldsymbol{T}\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{P}}\right)_{\boldsymbol{T}} + \boldsymbol{V}$$

From Maxwell, we have:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

So, we have:

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

This result shows that, for an ideal gas ($PV = nRT$):

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{V} \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = \frac{-nRT}{V} + V \neq f(P)$$

The Gibbs-Helmholtz Equation

The following is a very important derivation, which shows how ΔG can be obtained from a measurement of ΔH for a closed system of fixed composition (such as a chemical reaction occurring in a closed container).

We have:

$$G \equiv H - TS \Rightarrow$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Therefore, we have:

$$G = H + T\frac{dG}{dT}$$

Or, this is:

$$GdT = HdT + TdG$$

If we divide through by T^2, we get:

$$\frac{TdG - GdT}{T^2} = -\frac{H}{T^2}dT$$

From calculus, we know: $d(x/y) = (ydx - xdy)/y^2$, so that:

$$\frac{d(G/T)}{dT} = -\frac{H}{T^2}$$

For an isobaric change of state of a closed system of fixed composition:

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2}$$

Alternatively, we could have started with the fundamental equation:

$$dG = -SdT + VdP$$

Since: $= (H - G)/T$, we could write:

$$dG = -\frac{(H - G)}{T}dT + VdP$$

Thus, at constant pressure:

$$dG = -\frac{(H - G)}{T}dT$$

Or, this is:

$$TdG - GdT = -HdT$$

If we divide now by T^2, we get:

$$\frac{\boldsymbol{TdG - GdT}}{\boldsymbol{T^2}} = \frac{\boldsymbol{-HdT}}{\boldsymbol{T^2}}$$

Or, this is:

$$\boldsymbol{d(G/T)} = \frac{\boldsymbol{-HdT}}{\boldsymbol{T^2}} = \boldsymbol{Hd(1/T)}$$

This leads to either:

$$\left\{\frac{\boldsymbol{\partial(\Delta G/T)}}{\boldsymbol{\partial(1/T)}}\right\}_{\boldsymbol{P,n_i}} = \Delta\boldsymbol{H}$$

Or to:

$$\left\{\frac{\boldsymbol{\partial(\Delta\, G/T)}}{\boldsymbol{\partial(T)}}\right\}_{\boldsymbol{P,n_i}} = -\frac{\Delta\boldsymbol{H}}{\boldsymbol{T^2}}$$

An equivalent pair of equations can be developed for the Helmholtz Free Energy $\boldsymbol{A}$:

$$\left\{\frac{\boldsymbol{\partial(\Delta A/T)}}{\boldsymbol{\partial(1/T)}}\right\}_{\boldsymbol{V,n_i}} = \Delta\boldsymbol{U}$$

Or to:

$$\left\{\frac{\boldsymbol{\partial(\Delta A/T)}}{\boldsymbol{\partial(T)}}\right\}_{\boldsymbol{V,n_i}} = -\frac{\Delta\boldsymbol{U}}{\boldsymbol{T^2}}$$

STATISTICAL THERMODYNAMICS

Background

In the previous handout, the Kinetic Theory of Gases (KTG) provided an elemental, physical understanding of important thermodynamic properties, such as pressure, temperature and internal energy. While startlingly simplistic, KTG does give an intuitive feel for the FL. The SL, however, cannot be intuited from KTG.

Historically, the FL was readily accepted largely because of its intuitive basis (i.e., it stems from the idea of mass and energy balances). This was far from the case for the SL, even after entropy was deduced to be a state function, as is internal energy!

Understanding the SL was facilitated by *classical* statistical mechanics that introduced probability theory and the idea that equilibrium corresponded to the most probable of all possible states available to the system. But understanding the exact nature – what distinguishes each of these states – awaited the advent of *quantum mechanics* and the idea that the energy levels of individual atoms are actually quantized, possessing only specific energy levels. Each site of a lattice, for example, can now be understood to be in one of many distinct energy states and assigned a probability of occurrence. As a result, many different arrangements were understood to be possible among all the atoms of the system. The most probable arrangement could now be computed and accepted as a quantitative measure of the maximum degree of thermal disorder, providing a link to the macroscopic property of thermal entropy.

Earlier in this handout, temperature was seen to be a conjugate of the entropy function – this result deduced from purely on the logic of the combined FL and SL. Statistical thermodynamics gives us yet another interpretation of temperature – in addition to that provided by KTG and the Ideal Gas Law. It provides the basis for the Third Law (TL) which asserts that the entropy of a pure, stoichiometric, perfectly ordered crystal is zero at 0 degrees K.

The idea of zero absolute temperature was first deduced by extrapolating volume to zero in the Ideal Gas Law. Then, further confirmation from the combined FL and SL was deduced based on analysis of the Carnot cycle as the lowest temperature whereby 100 % efficiency could be obtained. Finally a third confirmation is given by the combination of classical thermodynamics (i.e., the FL and SL) and statistical mechanics, where a key parameter (the Lagrange multiplier $\boldsymbol{\beta}$) is found rigorously to be a singular function of absolute temperature.

Macro- and Microstates

We first need to distinguish the *macrostate* and the *microstate*. The former is, in classical thermodynamics, called a *state*, which is characterized by only a few state properties (viz.: $\boldsymbol{T}$, $\boldsymbol{P}$, $\boldsymbol{U}$ …). A *microstate* of a system characterizes all the particles in the system at a particular time – we must specify the *position* and *velocity* of each atomic species of the system:

- While equilibrium appears to be static on a macroscopic scale – appearing to be in a state of rest – it is actually dynamic, where all atomic species ($\boldsymbol{T} > 0$°K) are in motion, with their configuration changing constantly.
- The property of the macrostate is considered to be an average over all its properties in the microstates experienced by the system.
- The time-average of the properties of a system is assumed to be equivalent to the instantaneous average over the totality of microstates available to the system.
- Measurement of a macroscopic property captures an average in all of the microstates experienced by the system during the time of observation.

To quantify the macroscopic average of a property from consideration of the microscopic requires:

1. The property of each microstate;
2. Knowledge of which microstate the system can be in; and
3. The probability that the system will be in a given microstate.

Types of disorder

The thermodynamic (macro) state of a system is established by a macroscopic measuring of state properties, such as $\boldsymbol{U}$, $\boldsymbol{V}$, $\boldsymbol{x_i}$, in addition to specifying $\boldsymbol{T}$ and $\boldsymbol{P}$. Microscopically, this state is comprised of a large number of atoms, each one in one of several quantum states available to a particular system. This situation is characterized by a high degree of *energy*, or *thermal disorder*. If the atoms are also dissimilar, there are many different ways to arrange the lattice, which contributes additionally a degree of *chemical disorder*. The first type of disorder is quantified as thermal entropy, and the second as *configurational entropy*. The state of thermal and chemical equilibrium, in turn, is associated with both types of disorder, quantified as the most probable distribution of all possibilities, being at a maximum.

Determination of the Microstates of a Macrostate

We want to illustrate the difference between the microstates possible for a given macrostate. Consider a pure crystal with three distinguishable lattice sites A, B and C each containing atoms. Now consider three identical (hence, distinguishable) particles – these can be considered to be electrons – capable of possessing energy of one of four quantized energy levels:

1. A ground level at zero relative energy, where: $\boldsymbol{\varepsilon_0 = 0 \cdot u}$;
2. Level 1 with: $\boldsymbol{\varepsilon_1 = 1 \cdot u}$;
3. Level 2 with: $\boldsymbol{\varepsilon_2 = 2 \cdot u}$; and
4. Level 3 with: $\boldsymbol{\varepsilon_3 = 3 \cdot u}$**.**

So, we have a situation of three particles taking on one of four possible energy levels.

Now, we want to consider all the number of ways the three particles can be associated (or, reside) on the lattice sites. For simplicity in the present analysis, we want to keep the total energy constant at: $\boldsymbol{U = 3u}$. Figure HII.2 shows three different distributions are possible, each with: $\boldsymbol{U = 3u}$.

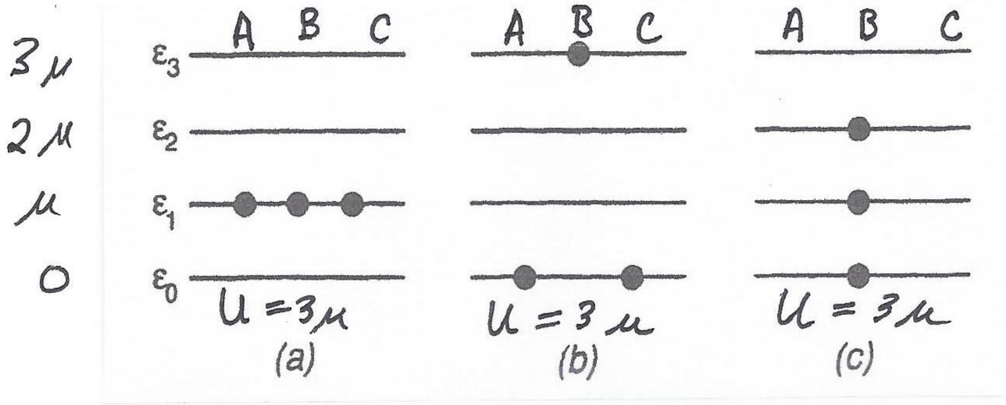


Figure HII.2 – The distribution of particles among energy levels in a system of constant energy.

By *distribution* is meant a distinct combination of the particles of the energy levels to achieve the total energy $\boldsymbol{U}$. Each distribution must achieve the same total energy $\boldsymbol{U}$. In our example, for Distribution *a*, only $\boldsymbol{\epsilon_1 = u}$ is employed; for Distribution *b*, one particle is at $\boldsymbol{\epsilon_3}$ and the other two are at the ground level $\boldsymbol{\varepsilon_0}$, and finally, for Distribution *c*, each of the three particles are in a different energy level, but where the total is $\boldsymbol{U}$.

But, because the sites are considered distinguishable, i.e., a site with an atom possessing an electron of one energy level is distinguishable from another site with an atom possessing an electron of a different energy level, there is the possibility of several different arrangements of the lattice sites. Figure HII.3 shows all possible arrangements.

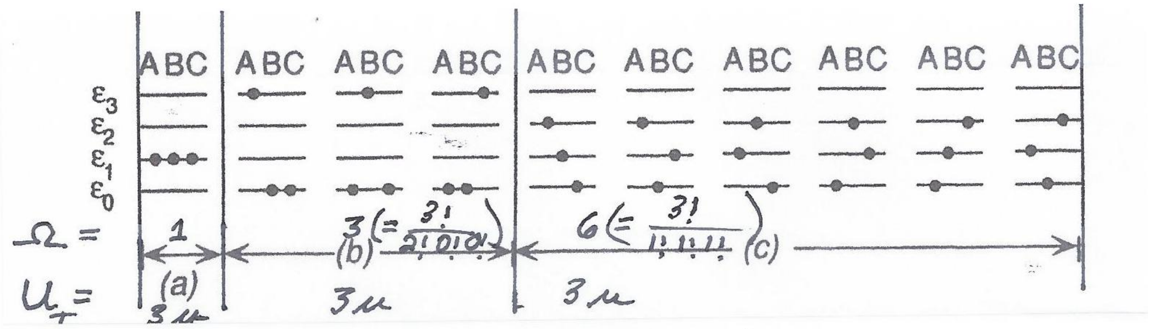


Figure HII.3 – Illustration of the complexions or microstates within distributions of particles among energy levels in a system of constant energy of $\boldsymbol{U}=\boldsymbol{3u}$. There are three different distributions (*a*, *b*, *c*) each with a different *Ω*.

At issue is to determine how many different distinguishable arrangements are possible:

Distribution a – - Here, there is only one arrangement for this distribution; i.e., interchanging the particles, all at energy level$\boldsymbol{\epsilon_1 = u}$, among the three lattice stesa does not produce a different arrangement.

Distribution b – Any of the three distinguishable lattice sites can be occupied by the particles of energy $\boldsymbol{3u}$, and the remaining two sites are each occupied by a particle of the ground state energy level. As interchange of the particles of zero energy does not produce a different arrangement, there can only be three arrangements.

Distribution c – Any of the three distinguishable lattice sites can be occupied by the particles of energy $\boldsymbol{2u}$, and either of the two remaining sites can be occupied by the particles of energy $\boldsymbol{1u}$, and the single remaining site is occupied by the particles of zero energy. The number of distinguishable arrangements in all thus is:$3 \cdot 2 \cdot 1 + 3! = 6$.

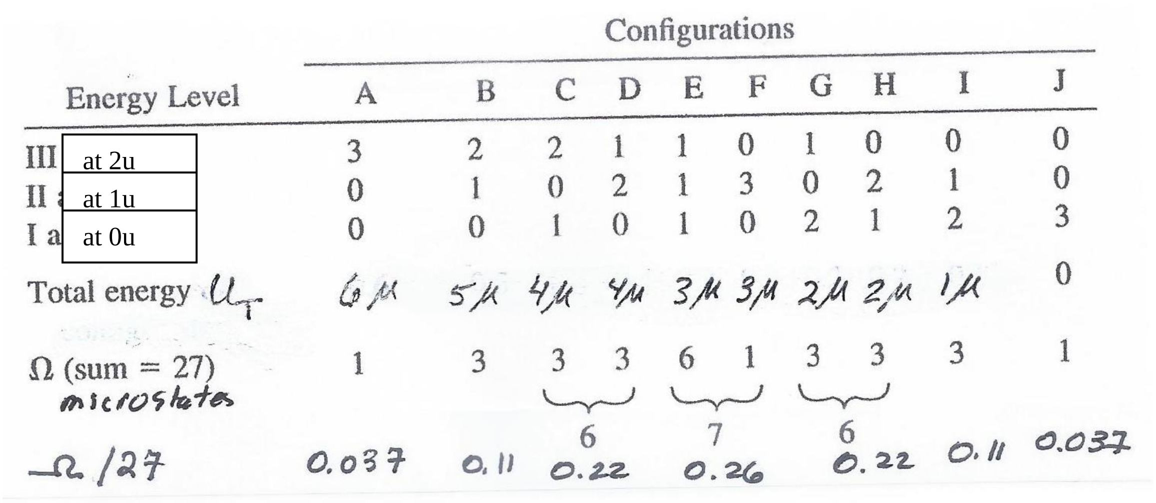
In all, there are 10 distinguishable ways in which three particles can be placed, keeping the total energy of the system of three sites equal to $\boldsymbol{U = 3u}$. Each arrangement is called a *microstate*, and all 10 correspond to a single *macrostate*.

In Figure HII.3, the following formula is invoked, corresponding to the total number of microstates $\boldsymbol{\Omega}$ for a given distribution (where it is noted that 0! = 1):

$$\boldsymbol{\Omega = \frac{n!}{n_0!\, n_1!\, n_2! \ldots n_i!} = \frac{3!}{n_0!\, n_1!\, n_2!\, n_3!}}$$

While, in the previous discussion, the total energy level is $= \boldsymbol{3u}$, in reality, we want to consider other total energy levels for the system; e.g., $\boldsymbol{U = 0, 1u, 2u, 3u, 4u,}$ ...In this case, we would get additional microstates depending on the total energy levels considered. If $\boldsymbol{U}$ is not held constant, the total number of microstates $\boldsymbol{\Omega_T}$ is obviously much greater. Similarly, as the number of atoms per lattice site increases, $\boldsymbol{\Omega}$ increases. For one mole of atoms (= 6.023 10^{23} atoms) then *n!* is an inconceivably large number.

For simplicity, we are going to now consider just three energy levels (ground level, $\boldsymbol{u}$ and $\boldsymbol{2u}$). So, for $\boldsymbol{U = 3u}$,we still have Distributions *a* and *c* in Figure HII.3, for which $\boldsymbol{\Omega = 1}$ and **6**, respectively. These two distributions for $\boldsymbol{U = 3u}$ are shown in the following table (HII.1) as Columns *E* and *F*.



	Configurations									
Energy Level	A	B	C	D	E	F	G	H	I	J
III at 2u	3	2	2	1	1	0	1	0	0	0
II at 1u	0	1	0	2	1	3	0	2	1	0
I at 0u	0	0	1	0	1	0	2	1	2	3
Total energy U_T	6μ	5μ	4μ	4μ	3μ	3μ	2μ	2μ	1μ	0
Ω (sum = 27) microstates	1	3	3	3	6	1	3	3	3	1
			6		7		6			
Ω /27	0.037	0.11	0.22		0.26		0.22		0.11	0.037

Table HII.1 Possible Distributions of Three Particles Among Three Different Quantum Energy Levels and Six different Total Energy Levels
($\boldsymbol{U = 0, 1u, 2u, 3u, 4u, 5u}$ **and 6u**).

The Microcanical Ensemble, the Canonical Ensemble and the Partition Function

In an isolated system of $\boldsymbol{n}$ particles in a volume $\boldsymbol{V}$, with a fixed total energy $\boldsymbol{U}$, each of the microstates can only have the same total energy. A basic assumption in statistical thermodynamics is that all microstates corresponding to the same total energy are equally probable. This particular set of microstates for a given total energy is called a *microcanical ensemble*. Corresponding to each energy state will be a number of quantum states. The totality over multiple energy states is: $\sum \boldsymbol{\Omega}$, for which all the quantum states possible for the system is termed the *canonical ensemble*. However, microstates corresponding to different energy/temperature levels are *not* equally probable.

Consider a molar volume of a *pure* crystal (i.e., one containing only one atomic specie). The $\boldsymbol{n}$ atoms in the crystal have a total energy $\boldsymbol{U}$. All the atoms do not necessarily have the same energy level, as fluctuations will occur whining the crystal. These energies are quantized, so that the atoms can only have discrete energy levels ($\boldsymbol{\varepsilon_0, \varepsilon_1,}$ etc.) and no values in between. The question occurs: How may atoms occupy each state? How many atoms are associated with each of the discrete energy levels available to the system?

At first glance, it would appear that the crystal at a minimum average energy state would have all atoms in the ground state ($\boldsymbol{\varepsilon_0}$) so that for the crystal $\boldsymbol{U = n\varepsilon_0}$. However, this ignores the extremely important contribution of (thermal) disorder, or entropy, in determining the thermal equilibrium state. Here, the thermal entropy is due to random mixing of atoms of different energy states due to the fact that these energy states are discrete (i.e., numbered) and the fact that the atoms (while all of the same atomic specie) are distinguishable from the point of view of energy. The state of thermal equilibrium corresponds to a maximum value of these mixing, hence, leading to occupancy of states other than the ground state.

The Boltzmann Hypothesis

Boltzmann expressed the relationship between the entropy of a system in a given state and the probability of existence of the given state. In this way, it now possible to calculate the entropy by calculating the probability of different states from analysis of the various distributions possible, and thereby link classical and statistical thermodynamics:

$$\boxed{\boldsymbol{S = k \ln \Omega}}$$

In the above equation, $\boldsymbol{k}$ is the Boltzmann constant.

The expression for entropy as merely a logarithm of the total number of distributions is a simple, but brilliant insight. This characterization can be understood by considering the mathematical nature of the microstate versus the macrostate. For the macrostate, entropy is an extensive state property, so that combination of two systems results in the *addition* of the individual values of the entropy. But, for the microstate, it is quantified by probability, so combining two systems must be a *product* of the number of microstates for each. Because of the additive nature of entropy as a state property and the multiplicative nature of thermodynamic probability, the function that relates the two had to be a logarithm!

The most probable distribution of atoms possessing one of the discrete energy levels is obtained by determining the set of numbers of atoms in each energy state that maximizes $\boldsymbol{\Omega}$. For $\boldsymbol{n}$ (on the order of the size of 1 mole), $\boldsymbol{\Omega_{max}}$ is significantly larger than the sum of all other arrangements $\boldsymbol{\Omega_{total}}$, so:

$$\boldsymbol{S = k \ln \Omega_{\mathrm{max}}}$$

For this maximization, we need to consider the mass and energy balances in terms of a *variation* in the number of atoms in each energy state: $\boldsymbol{\delta n_0}, \boldsymbol{\delta n_1}, \boldsymbol{\delta n_2}, \dots \boldsymbol{\delta n_i}$, as it is this variation, not the number themselves ($\boldsymbol{n_0}, \boldsymbol{n_1}, \dots$) that allows for the maximization to be calculated.

The energy balance is:

$$\boldsymbol{U = \text{constant} = n_0\varepsilon_0 + n_1\varepsilon_1 + \cdots n_i\varepsilon_i = \sum_{i=0}^{n} n_i\varepsilon_i = n\wp_i\varepsilon_i}$$

Here,

$$\boldsymbol{\wp_i \equiv \frac{n}{n_i}}$$

Where

$$\sum \boldsymbol{\wp_i}=1$$

In the above equation, $\boldsymbol{\wp_i}$ is the probability of atoms being in a particular energy state $\boldsymbol{i}$.

The mass balance is:

$$\boldsymbol{n = \text{constant} = n_0 + n_1 + \cdots n_r = \sum_{i=0}^{n} n_i = n\sum \wp_i}$$

As seen earlier, the formula for determining the number of arrangements for a distribution is:

$$\boldsymbol{\Omega = \frac{n!}{n_0!\,n_1!\,n_2!\dots n_i!}}$$

For $\boldsymbol{n}$ being large, Stirling’s Approximation (for large $\boldsymbol{x}$) greatly simplifies this equation:

$$\ln \boldsymbol{x}! \cong \boldsymbol{x} \ln \boldsymbol{x} - \boldsymbol{x}$$

So, we have:

$$\ln \Omega = \boldsymbol{n} \ln \boldsymbol{n} - \boldsymbol{n} - \sum_{i=0}^{i=r} (\boldsymbol{n}_i \ln \boldsymbol{n}_i - \boldsymbol{n}_i) =$$

$$-\sum_{i=0}^{i=r} \frac{\boldsymbol{n}_i}{\boldsymbol{n}} \ln \frac{\boldsymbol{n}_i}{\boldsymbol{n}} = -\sum \wp_i \ln \wp_i$$

But, as stated earlier, we need to vary $\boldsymbol{n_i}$; viz.: $\boldsymbol{\delta n_i}$. To do this, we must restate the energy and mass balances:

$$\boldsymbol{\delta U} = \sum_i \boldsymbol{\varepsilon}_i \boldsymbol{\delta}\, \boldsymbol{n}_i = \mathbf{0}$$

$$\boldsymbol{\delta n}_i = \sum_i \boldsymbol{\delta n}_i = \mathbf{0}$$

Finally, to maximize $\boldsymbol{\Omega}$, $\boldsymbol{\delta ln\Omega = 0}$, or:

$$-\sum \boldsymbol{\delta n}_i \ln \boldsymbol{\delta n}_i = \mathbf{0}$$

The solution for maximization of $\boldsymbol{\Omega}$ is found by the Technique of Lagrange Multipliers. The result is:

$$\frac{\boldsymbol{n}_i}{\boldsymbol{n}} = \frac{\boldsymbol{e}^{(-\boldsymbol{\beta}\boldsymbol{\varepsilon}_i)}}{\sum_i \boldsymbol{e}^{(-\boldsymbol{\beta}\boldsymbol{\varepsilon}_i)}} = \wp_i$$

In the above equation, the numerator is called the *Partition Function* $\wp$**:**

$$\wp = \sum_i e^{(-\beta\varepsilon_i)}$$

The equation:

$$\wp_i = \frac{e^{(-\beta\varepsilon_i)}}{\sum_i e^{(-\beta\varepsilon_i)}} = \frac{n_i}{n}$$

Gives the distribution of atoms (or particles) in the various discrete energy levels that maximizes Ω. The nature of this solution is exponential. Occupancy of these levels is such that it decreases exponentially with energy level – there are fewer atoms (or particles) associated with the higher energy levels than with the lower. This is shown in Figure HII.4.

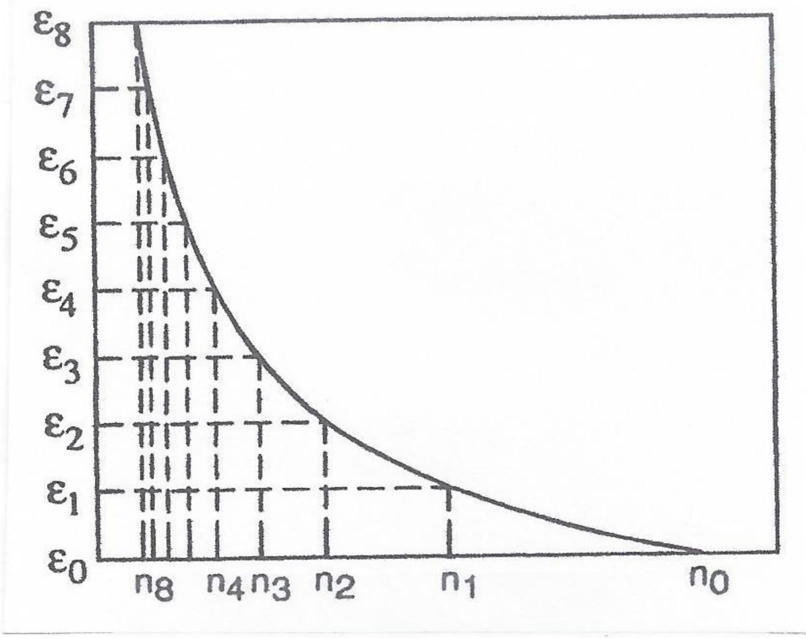


Figure HII.4 – Schematic representation of the most probable distribution of particles among quantized energy levels.

One of the startlingly simple and elegant result of this analysis is proof on combining classical and statistical thermodynamics that the Lagrange multiplier $\boldsymbol{\beta}$ is in fact actually temperature:

$$\boldsymbol{\beta = -\frac{1}{kT}}$$

This provides a third interpretation of temperature! The proof is as follows.

From classical thermodynamics, we have:

$$\boldsymbol{dU = TdS - PdV}$$

Thus:

$$\boldsymbol{\left(\frac{\partial U}{\partial S}\right)_V = T}$$

Or

$$\boldsymbol{\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}}$$

From our earlier analysis of $\boldsymbol{\wp_i}$:

$$\boldsymbol{\ln\Omega = -\sum\frac{n}{n_i}\ln\frac{n}{n_i} = -\sum\wp_i\ln\wp_i = -\sum\wp_i(\ln\wp_i)}$$

But:

$$\boldsymbol{\ln\wp_i = -\ln\wp - \beta\varepsilon_i}$$

So:

$$\ln \boldsymbol{\Omega} = -\sum \wp_i(-\ln \wp_i - \boldsymbol{\beta\varepsilon_i}) =$$

$$\sum \wp_i \ln \wp_i + \sum \wp_i \boldsymbol{\beta\varepsilon_i}$$

Since $\boldsymbol{\beta}$ and $\boldsymbol{\varepsilon_i}$ are constants, and setting $U = \sum \wp_i \boldsymbol{\varepsilon_i}$, we have:

$$\ln \boldsymbol{\Omega} = \ln \wp + \boldsymbol{\beta U}$$

Finally:

$$\boldsymbol{k} \ln \boldsymbol{\Omega} = \boldsymbol{S} = \mathbf{k}\ln \wp + \boldsymbol{k\beta\varepsilon_i}$$

Now, we invoke calculus manipulations (see HI). First, we take the differential of this function for $\boldsymbol{S}$ with respect to $\boldsymbol{U}$:

$$\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{U}}\right)_{\boldsymbol{V}} = \frac{\boldsymbol{k}}{\wp}\left(\frac{\partial \wp}{\partial \boldsymbol{U}}\right)_{\boldsymbol{V}} + \boldsymbol{k\beta} + \boldsymbol{kU}\left(\frac{\partial \boldsymbol{\beta}}{\partial \boldsymbol{U}}\right)_{\boldsymbol{V}}$$

From the *chain rule*:

$$\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{U}}\right)_{\boldsymbol{V}} = \frac{\boldsymbol{k}}{\wp}\left(\frac{\partial \wp}{\partial \boldsymbol{\beta}}\right)_{\boldsymbol{V}}\left(\frac{\partial \boldsymbol{\beta}}{\partial \boldsymbol{U}}\right)_{\boldsymbol{V}} + \boldsymbol{k\beta} + \boldsymbol{kU}\left(\frac{\partial \boldsymbol{\beta}}{\partial \boldsymbol{U}}\right)_{\boldsymbol{V}}$$

Now, we want to differentiate the partition function $\wp$ with respect to $\boldsymbol{\beta}$**:**

$$\left(\frac{\partial \wp}{\partial \boldsymbol{\beta}}\right)_{\boldsymbol{V}} = -\sum_{\boldsymbol{i}} \boldsymbol{\varepsilon_i e^{(-\beta\varepsilon_i)}}$$

But, we have:

$$\boldsymbol{e^{(-\beta\varepsilon_i)} = \wp\wp_i}$$

Also, we know:

$$\boldsymbol{\sum \wp_i\varepsilon_i = U}$$

So that, we have:

$$\boldsymbol{\left(\frac{\partial\wp}{\partial\beta}\right)_V = -\sum \wp\wp_i\varepsilon_i = -\wp\sum \wp_i\varepsilon_i}$$

$$\boldsymbol{\left(\frac{\partial\wp}{\partial\beta}\right)_V = -\wp U}$$

Finally, we have, on inserting for the above:

$$\boldsymbol{\left(\frac{\partial S}{\partial U}\right)_V = \frac{k}{\wp}(-\wp U)\left(\frac{\partial\beta}{\partial U}\right)_V + k\beta + kU\left(\frac{\partial\beta}{\partial U}\right)_V =}$$

$$\boldsymbol{-kU\left(\frac{\partial\beta}{\partial U}\right)_V + k\beta + kU\left(\frac{\partial\beta}{\partial U}\right)_V =}$$

$$\boldsymbol{k\beta = \frac{1}{T} \Rightarrow}$$

$$\boxed{\boldsymbol{\beta = \frac{1}{kT}}}$$

The foregoing analysis to arrive at the partition function as a function of $\boldsymbol{\beta}$ and $\boldsymbol{\varepsilon_i}$ was based on holding $\boldsymbol{U}$ (which means $\boldsymbol{T}$) constant. But, given the result that $\boldsymbol{\beta = 1/kT}$, we can now see how the distribution changes with $\boldsymbol{T}$, which is equivalent to changes in $\boldsymbol{U}$. Figure HII.5 shows this qualitatively.

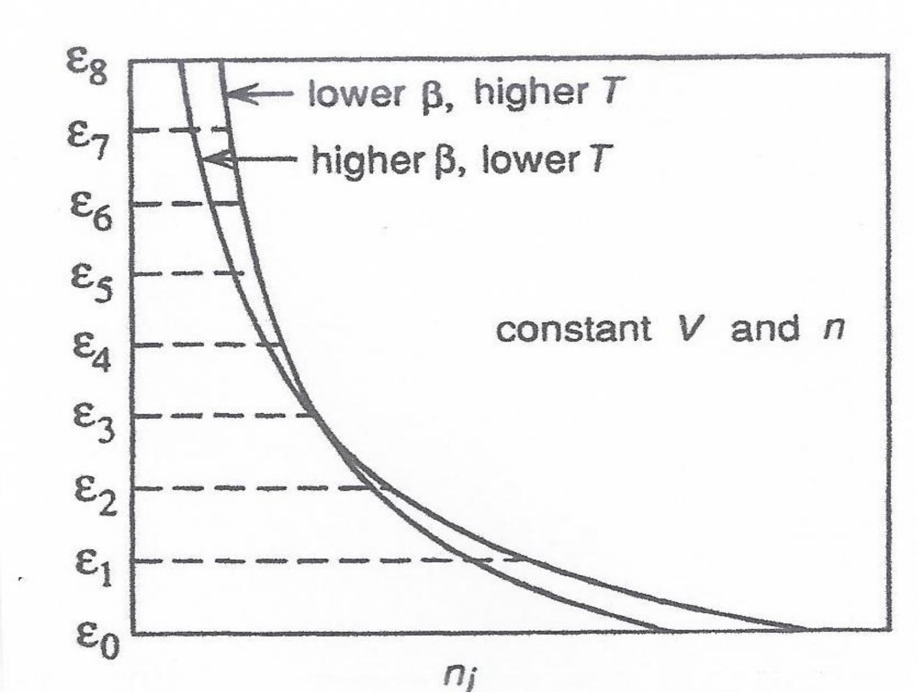


Figure HII.5 – The influence of temperature on the most probable distribution of particles among energy levels in a closed system of constant volume.

It is now seen that higher temperatures shift more atoms/particles to the higher energy levels than lower temperatures. From KTG, this stands to reason – as temperature increases, the average energy of the atoms/particles of a system directly increases.

Production of Entropy in Attainment of Equilibrium

We know from everyday experience that the transfer of heat from a body at a higher temperature to one at a lower temperature is irreversible. This is also deduced from classical thermodynamics as delineated in HI, where entropy increases as a result of this heat transfer. Now, from the point of view of the microstate, we see that why this is so. What is considered classical thermodynamics to be *impossible*, or *irreversible* is seen simply to be *improbable*!

The following analysis also shows clearly that entropy is at a maximum when thermal equilibrium is achieved. Consider two closed Systems A and B. Let the total energy be $\boldsymbol{U_A}$ and the total number of complexions for A be $\boldsymbol{\Omega_A}$, and $\boldsymbol{U_B}$ and $\boldsymbol{\Omega_B}$ for B, respectively.

When thermal contact is made between A and B, the product $\boldsymbol{\Omega_A \Omega_B}$ will not have a maximum value if heat begins to transfer between A and B. Heat continues to one system from the other, increasing $\boldsymbol{\Omega_A \Omega_B}$ until a maximum is reached, whence:

$$\boldsymbol{\delta \ln \Omega_A \Omega_B = 0}$$

But:

$$\boldsymbol{\delta \ln \Omega_A = \frac{\delta q_A}{kT_A}}$$

And

$$\boldsymbol{\delta \ln \Omega_B = \frac{\delta q_B}{kT_B}}$$

Furthermore, for a constant total energy:

$$\boldsymbol{\delta q_A = -\,\delta q_B}$$

Thus:

$$\boldsymbol{\delta \ln \Omega_A \Omega_B = \delta \ln \Omega_A + \delta \ln \Omega_B = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\frac{\delta q}{k}}$$

It is now readily seen at the maximum: $\boldsymbol{T_A = T_B}$, which corresponds to the classical definition of thermal equilibrium!

Configurational Entropy

Consider the mixing effect of two dissimilar atomic Species A and B, resulting in an ideal solution, where the positioning of the mix of atoms on a lattice is completely random. (It is to be noted that for an ideal solution, there is no energy – enthalpy - of mixing; all configurations are at the same energy level and are equally probable.) For one mole of atoms (= 6.023 10^{23} atoms) we have:

$$\boldsymbol{\Omega = \frac{n!}{n_A!\, n_B!}}$$

This equation may or may not seem obvious. One way to arrive at this equation is to realize that there are $\boldsymbol{n}$ ways of introducing the atoms onto the lattice, one at a time. The first atom can be chosen at random from among $\boldsymbol{n_A}$ and $\boldsymbol{n_B}$, in *n* different ways. The second atom may be chosen in $\boldsymbol{n\text{-}1}$ different ways from the remaining pool of $\boldsymbol{n\text{-}1}$ atoms, and so forth. The total number of ways of placing all the atoms onto the lattice is:

$$\boldsymbol{n(n-1)(n-2)\ldots(3)(2)(1) = n!}$$

However, not all of the configurations are distinguishable! To account for this, we must divide by the number of different ways that the $\boldsymbol{n_A}$ atoms can be distributed on their sites – re-arranging atoms of $\boldsymbol{n_A}$ labeled 1, labeled 2, … can be done $\boldsymbol{n_A!}$ number of ways. Since these are all indistinguishable – all being A atoms, the total number of configurations must be divided by this amount: $\boldsymbol{n_A!}$ for the indistinguishable A atoms, and by $\boldsymbol{n_B!}$ for the indistinguishable B atoms. What remains is the number of ways of arranging $\boldsymbol{n}$ atoms, two at a time.

So, now we have:

$$\boldsymbol{S_{mix} = k \ln \Omega = \mathbf{k} \ln \frac{n!}{n_A!\, n_B!}}$$

Or

$$\boldsymbol{S_{mix} = k[\ln n! - \ln n_A! - \ln n_B!]}$$

This equation can be simplified as before using Stirling's Approximation, where:

$$\boldsymbol{n! \cong n^n e^{-n} (2\pi n)^{1/2}}$$

Or

$$\boldsymbol{\ln n! \cong n \ln n - n}$$

So that:

$$\boldsymbol{S_{mix} = -k\left[n_A \ln\frac{n_A}{n} + n_B \ln\frac{n_B}{n}\right]}$$

Or, in terms of *mole fraction*, where: $\boldsymbol{x_A = n_A/n}$; $\boldsymbol{x_B = n_B/n}$, we have:

$$\boldsymbol{S_{mix} = -R[x_A \ln x_A + x_B \ln x_B]}$$

In the above equation, **R (= k*n*)** is the Universal gas Constant; taking $\boldsymbol{n}$ to be one mole of atoms, we have the *intensive* entropy of mixing.

Obviously, this formula can be generalized for the entropy of mixing of one mole of an ideal solution of $\boldsymbol{i}$ components (where the underline signifies the intensive property):

$$\boxed{\boldsymbol{\underline{S} = -R\sum_i x_i \ln x_i}}$$

Combination of Thermal and Configurationsl Entropy

The total entropy of a system consists of the sum of the thermal entropy $\boldsymbol{S_{th}}$ and the configurational entropy, or entropy of mixing $\boldsymbol{S_{mix}}$:

$$\boldsymbol{S_{total} = S_{th} + S_{mix} = k \ln \Omega_{th} + k \ln \Omega_{mix} = k \ln(\Omega_{th}\Omega_{mix})}$$

Consider the mixing of two closed systems, each containing only one atomic specie, but not the same specie between the two systems. If the systems on contact are also at different temperatures, in addition to the diffusion to the diffusion of dissimilar atom into each system, there is the transfer of heat until chemical and thermal equilibrium – that is, complete equilibrium – is attained in the transition from State 1 (pure A at $\boldsymbol{T_A}$ and pure B at $\boldsymbol{T_B}$ versus State 2, consisting of A & B in solution in a lattice at a mutual temperature $\boldsymbol{T_{mix}}$. The net change in total entropy is:

$$\Delta \boldsymbol{S}_{total} = \boldsymbol{S}_2 - \boldsymbol{S}_1 = \boldsymbol{k} \ln \frac{\boldsymbol{\Omega}_{th,2}\boldsymbol{\Omega}_{mix,2}}{\boldsymbol{\Omega}_{th,1}\boldsymbol{\Omega}_{mix,1}} =$$

$$\boldsymbol{k} \ln \frac{\boldsymbol{\Omega}_{th,2}\boldsymbol{\Omega}_{mix,2}}{\boldsymbol{\Omega}_{th,1}}$$

Note that $\boldsymbol{\Omega}_{mix,1} = \mathbf{1} \cdot \mathbf{1} = \mathbf{1}$, since the systems are initially pure. Obviously, if both systems initially are at the same temperature, then:

$$\Delta \boldsymbol{S}_{total} = \ln \boldsymbol{\Omega}_{mix,2}$$

In point of fact, this is for the *ideal* mixing process – one where mixing does not involve a change in total energy of the combined systems per total number of atoms. Ideal mixing is hardly ever the result of the mixing of two atomic species! Instead, in most instances, $\boldsymbol{U}$ and $\boldsymbol{V}$ do change (whether positive or negative) on mixing, and this must involve the distribution of the particles among the various discrete energy levels. This is seen macroscopically not only in a measureable change in these state properties, but physically as a tendency of dissimilar species to either cluster (in the extreme, forming compounds) or to repel (clustering of like species, causing a mechanical mixture in the extreme, where the characteristics of the pure species are retained for the mixture). Nonetheless, in all cases, the equilibrium state of the system is that which, at a constant $\boldsymbol{U}$, $\boldsymbol{V}$ and $\boldsymbol{n}$, maximizes the product $\boldsymbol{\Omega}_{th}\boldsymbol{\Omega}_{mix}$.

The Barometric Equation Verified by Statistical Thermodynamics

As with KTG, we can derive the barometric equation from first principles by applying the partition function. Consider an isothermal column of gas of height $\boldsymbol{h}$. The potential energy of an atom at the top of the column relative to the bottom is the difference in the potential energy $\boldsymbol{mgh}$, as seen in Figure HII.6.

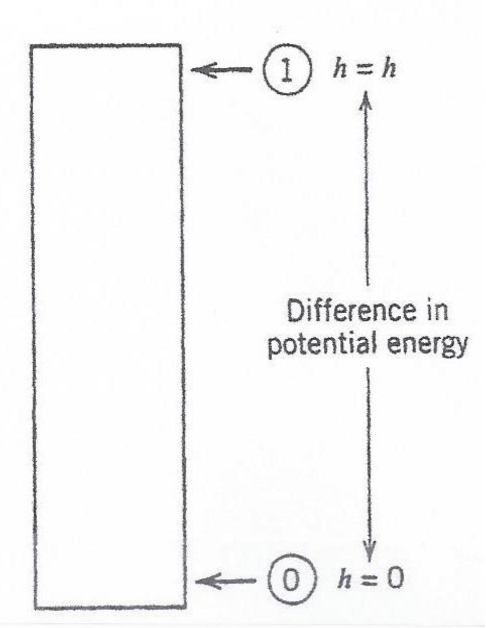


Figure HII.6 - Isothermal column of gas.

Consider two spaces of equal volume, one at the top of the column, and the other one at the bottom. The probability of finding any atom in the top ($\wp_{\mathbf{1}}$) relative to the bottom ($\wp_{\mathbf{0}}$) is:

$$\wp_{\mathbf{1}} = \frac{\mathbf{exp}(-\boldsymbol{E_1/kT})}{\wp}$$

And

$$\wp_{\boldsymbol{o}} = \frac{\mathbf{exp}(-\boldsymbol{E_o/kT})}{\wp} \Rightarrow$$

$$\frac{\wp_{\mathbf{1}}}{\wp_{\boldsymbol{o}}} = \mathbf{exp}(-(\boldsymbol{E_1} - \boldsymbol{E_o})/\boldsymbol{kT}) = \mathbf{exp}(-\boldsymbol{mgh/kT})$$

Because this ratio of probability applies to all the atoms at each location, $\boldsymbol{n_1}$and $\boldsymbol{n_0}$, we have:

$$\frac{\boldsymbol{n_1}}{\boldsymbol{n_o}} = \mathbf{exp}(-\boldsymbol{mgh/kT})$$

Now, consider the gas to be ideal, so that from the Ideal Gas Law applied to each location, we get:

$$\frac{P_1}{P_o} = \exp(-mgh/kT)$$

In the above equation, *m* is the mass of one atom and ***P*** is the pressure (not to be confused with probability (℘). Taking ***M*** to be one mole of atoms, we finally have the Barometric Equation:

$$\frac{P_1}{P_o} = \exp(-Mgh/RT)$$

Insight Into the Third Law

It is interesting to revisit entropy of mixing for the case of a perfect compound. By *perfect*, we mean mixing of Species A and Species B are in perfect accord as a compound, with no imperfections in its stoiciometry. Such an arrangement is shown in Figure HII.7.

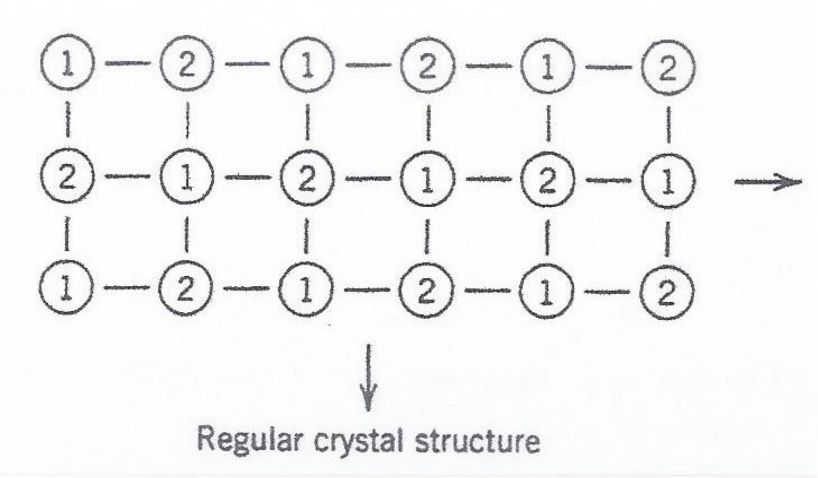


Figure HII.7 – Arrangement of atoms in a perfect compound.

Now, we want to reason as to the number of arrangements on forming this compound from pure A and pure B. Because we are following a stoiciometric formula (here A:B is 1:1) $\boldsymbol{\Omega}$ is equal to unity:

$$\boldsymbol{\Omega} = \frac{\boldsymbol{n_A}!\,\boldsymbol{n_B}!}{\boldsymbol{n_A}!\,\boldsymbol{n_B}!}$$

The only difference is the selection process: once an atom has been selected (say, from the upper left hand corner of the lattice) it follows that the sites immediately surrounding it must be of the other specie. The second atom selected is not drawn from the pool of the first atom selected, but the pool of the second specie. If the first atom chosen is A, it is selected from the pool of $\boldsymbol{n_A}$ atoms, but the second is from the pool of B atoms $\boldsymbol{n_B}$.The third atom must be selected from the pool of $\boldsymbol{n_A - 1}$ atoms, and the fourth atom from the pool of $\boldsymbol{n_B - 1}$ and so forth. Hence, the numerator, which accounts for the indistinguishability of the A atoms on the A sites and the B atoms on the B sites is also: $\boldsymbol{n_A}!\,\boldsymbol{n_B}$.

This result gives insight into the basis of the Third Law (TL). If two components of atomic species are, at absolute zero, combines to form a perfectly ordered crystal, the entropy change is zero. Thus, entropy must range from zero for the perfectly ordered crystal to $\boldsymbol{S_{mix}}$ for random mixing of an ideal solution.

Degeneracy

The equation given earlier for the partition function $\wp_{\boldsymbol{i}}$ can be modified from an accounting perspective, depending on how the arrangements are counted. Here, we distinguish the difference between energy *level* and energy *state*. A factor $\boldsymbol{g_i}$ can be introduced in the equation for partition function to account for the statistical weight of the energy level; i.e., at any one energy level $\boldsymbol{\mathcal{E}_i}$, there may be $\boldsymbol{g_i}$ states – all having the same energy, but different arrangements.

The probability a particle will be in a specific state is:

$$\wp_{\boldsymbol{i}} = \frac{\boldsymbol{exp(-\mathcal{E}_i/kT)}}{\wp}$$

In the above equation, $\wp$ is summed over all the states of the system; viz.: $\wp = \sum_i \boldsymbol{exp(-\mathcal{E}_i/kT)}$**.** On the other hand, the probability that a particle will be in a specified energy level is:

$$\wp_i = \boldsymbol{g_i} \frac{\boldsymbol{exp(-\mathcal{E}_i/kT)}}{\wp}$$

In the above equation, $\wp = \sum_i \boldsymbol{g_i exp(-\mathcal{E}_i/kT)}$, which is summed over all the levels.

This is merely an accounting procedure. With reference to Table HII.1, one can sum over each possible state, where all the sub-states within one energy level is assumed to be independent.

Alternatively, if one accounts for the number of sub-states in each energy level straight on, then the sum is over all energy levels.

So, referring to this table, the partition function evaluated as the sum over all the states of the system would have $\boldsymbol{\Omega = 27}$ terms in it, one for each of the 27 possible microstates.

The partition function evaluated as the sum over energy levels would have only 7 terms, one for each of the 7 energy levels. At each energy level, $\boldsymbol{g_i}$would equal the number of microstates for a given energy level. For example, the *b* level would have a degeneracy of 3.

Distinguishability of Particles

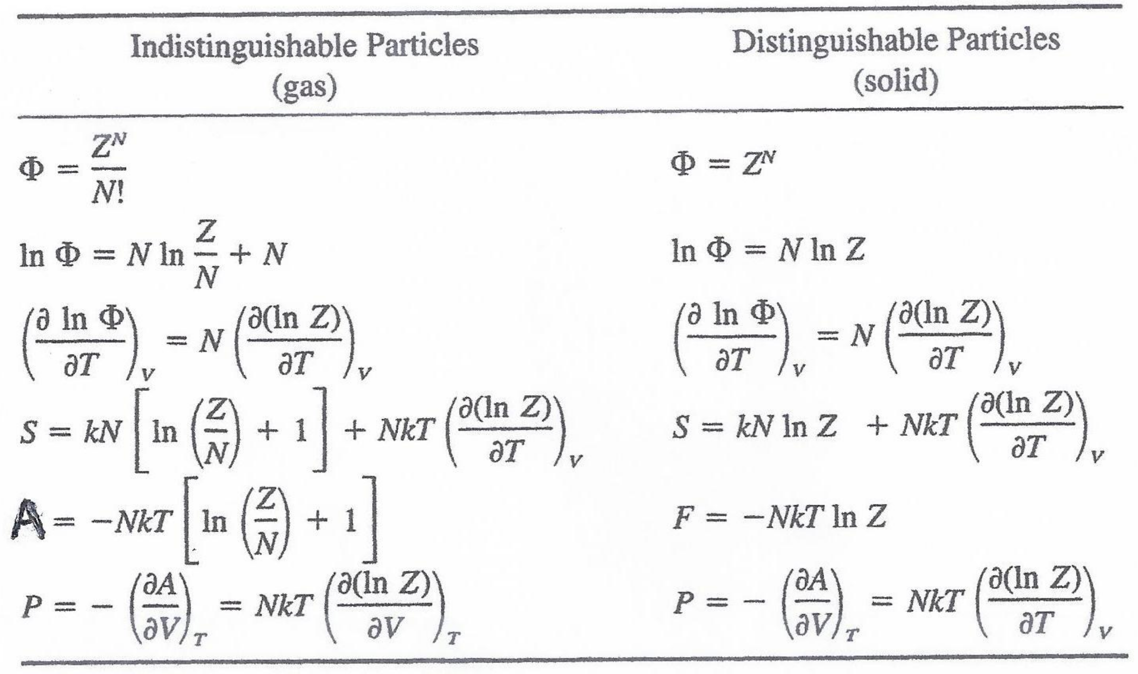
It is important to distinguish a gas from a solid in considering the question of distinguishability. It comes down to whether the atoms are *localized* or not. Atomic species in a crystal are localized; atomic species in a gas are not. In a solid (or liquid, which essentially is a solid, but with short range ordering) the atomic species vibrate about a fixed space, hence are localized, because they can have different vibrations corresponding to a thermal distinguishability among different species of the system. If the species are not interacting when combined, where there is no additional change in energy from any interaction, the so called *Grand Partition Function* (GPF) $\boldsymbol{\Phi}$ for the system of combined species is simply the partition function of the individual atoms, but where account is taken of the combination of energy states of the system of combined species:

$$\boldsymbol{\Phi}_{\mathbf{solids}\ \&\ liquids} = \wp^{\mathbf{n}}$$

For a gas, it is important to recognize that the individual species are *not* distinguishable. So, following the previous procedure to deduct for non-distinguishability, we have:

$$\mathbf{\Phi_{gas}} = \frac{\wp^{\mathbf{n}}}{\mathbf{n}!}$$

From the GPF, we can deduce the macrostate properties for $\boldsymbol{S}$, $\boldsymbol{A}$ and $\boldsymbol{P}$. These are shown in Table HII.2.



Indistinguishable Particles (gas)	Distinguishable Particles (solid)
$\Phi = \frac{Z^N}{N!}$	$\Phi = Z^N$
$\ln \Phi = N \ln \frac{Z}{N} + N$	$\ln \Phi = N \ln Z$
$\left(\frac{\partial \ln \Phi}{\partial T}\right)_V = N\left(\frac{\partial(\ln Z)}{\partial T}\right)_V$	$\left(\frac{\partial \ln \Phi}{\partial T}\right)_V = N\left(\frac{\partial(\ln Z)}{\partial T}\right)_V$
$S = kN\left[\ln\left(\frac{Z}{N}\right) + 1\right] + NkT\left(\frac{\partial(\ln Z)}{\partial T}\right)_V$	$S = kN \ln Z + NkT\left(\frac{\partial(\ln Z)}{\partial T}\right)_V$
$A = -NkT\left[\ln\left(\frac{Z}{N}\right) + 1\right]$	$F = -NkT \ln Z$
$P = -\left(\frac{\partial A}{\partial V}\right)_T = NkT\left(\frac{\partial(\ln Z)}{\partial V}\right)_T$	$P = -\left(\frac{\partial A}{\partial V}\right)_T = NkT\left(\frac{\partial(\ln Z)}{\partial T}\right)_V$

Table HII.2 – Partition function ($\boldsymbol{\Phi}$) for many ($\boldsymbol{N}$) particles based on the partition function for one particle ($\boldsymbol{z} = \wp_{\boldsymbol{i}}$).

This calculation is illustrated considering a system of *one particle*. We begin with the equation:

$$\boldsymbol{S} = \boldsymbol{k} \ln \wp + \frac{\boldsymbol{U}}{\boldsymbol{T}}$$

The internal energy of this one particle is:

$$U = \sum\nolimits_i \epsilon_i \wp_i = \sum_i \varepsilon_i \frac{\exp(-\epsilon_i/kT)}{\wp} = \frac{1}{\wp}\sum_i \varepsilon_i \exp(-\epsilon_i/kT)$$

We note that:

$$\wp = \sum_i \exp(-\epsilon_i/kT) \Rightarrow$$

$$\left(\frac{\partial \wp}{\partial T}\right)_V = \sum_i \exp(-\epsilon_i/kT)\frac{\epsilon_i}{kT^2} = \frac{1}{kT^2}\sum_i \varepsilon_i \exp(-\epsilon_i/kT)$$

This gives:

$$\sum_i \varepsilon_i \exp(-\epsilon_i/kT) = \left(\frac{\partial \wp}{\partial T}\right)_V kT^2$$

Therefore

$$U = \frac{1}{\wp} kT^2 \left(\frac{\partial \wp}{\partial T}\right)_V = kT^2 \left(\frac{\partial \ln \wp}{\partial T}\right)_V$$

Now, on substitution back in this equation for S, we get:

$$\boxed{S = k \ln \wp + kT \left(\frac{\partial \ln \wp}{\partial T}\right)_V}$$

Similarly, since the Helmholtz Free Energy is $A = U - TS$, we have:

$$\boxed{A = -kT \ln \wp}$$

What actually is $\wp$ for an ideal gas in terms of a mass $\boldsymbol{m}$ of the gas in terms of its kinetic energy? For this, we consider the simplest case, which involves the motion of this mass of one particle in a cubical box of dimensions $\boldsymbol{L \cdot L \cdot L}$, where its velocity is quantized. Here, we are considering only translation motion leading to kinetic energy (rotation, vibration, or electronic excitation are all ignored).

This velocity is quantized, having a wavelength in the x-direction defined by the DeBrogolie relationship (where $= \boldsymbol{2L/i}, \boldsymbol{i} =$ 1,2,3 ... , and $\boldsymbol{h}$ is Plank's constant :

$$\boldsymbol{mv = \frac{h}{\lambda}}$$

Consider the x-direction, then:

$$\boldsymbol{v_x = \frac{hi}{2mL}}$$

Its energy (noting $\boldsymbol{E_x = \frac{1}{2} m v_x^2}$) is:

$$\boldsymbol{E_x = \frac{h^2 i^2}{2mL}}$$

Therefore, the partition function in the x-direction becomes:

$$\wp_{\boldsymbol{x}} = \boldsymbol{\left(\frac{2\pi m k T}{h^2}\right)^{1/2} L}$$

Finally. For all three directions, we have:

$$\boxed{\wp_{\boldsymbol{xyz}} = \wp_{\boldsymbol{x}} \wp_{\boldsymbol{y}} \wp_{\boldsymbol{z}} = \wp = \boldsymbol{\left(\frac{2\pi m k T}{h^2}\right)^{3/2} V = \frac{V}{h^3} (2\pi m k T)^{3/2}}}$$

The pressure of an ideal, monatomic gas now can be calculated, as follows. The Helmholtz Free Energy (for one mole of gas) is:

$$\boldsymbol{A = -n_{Avogadro}kT\left(\ln\frac{\wp}{n_{Avogadro}} + 1\right)}$$

Since:

$$\boldsymbol{P = -\left(\frac{\partial A}{\partial V}\right)_T}$$

Then, we have:

$$\boldsymbol{P = n_{Avogadro}kT\left(\frac{\partial \ln \wp}{\partial V}\right)_T}$$

In the above equation:

$$\boldsymbol{\wp = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V}$$

In the above equation, $\boldsymbol{h}$ is Plank's constant.

Finally, the grand result, inserting for the partition function derived for translational motion of the gas particle, is:

$$\boldsymbol{P = \frac{n_{Avogadro}kT}{V} = \frac{RT}{V}}$$

Obviously this above result is none other than the Ideal Gas Law!

Since this is true, it is easy to show that for an ideal gas, the partial of internal energy with respect to volume, holding temperature constant is zero. We start with the fundamental equation:

$$dU = TdS - PdV$$

From this we find:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Then, from the fundamental equation:

$$dA = -SdT - PdV$$

We find:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Finally:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

We can already use the result given above, where the Ideal Gas Law resulted from employing the partition function in for the Helmholtz Free Energy. Here, we re-derive pressure employing the partition function directly:

$$\boldsymbol{P = n_{Avogadro}kT\left(\frac{\partial \ln \wp}{\partial V}\right)_T}$$

Where:

$$\boldsymbol{\wp_{xyz} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V}$$

From this expression, we find:

$$\boldsymbol{\left(\frac{\partial \ln \wp}{\partial V}\right)_T = \left(\frac{\partial \ln V}{\partial V}\right)_T = \frac{1}{V}}$$

So that, once again, using the expression for the partition function, we get the Ideal Gas Law:

$$\boldsymbol{P = n_{Avogadro}kT\left(\frac{1}{V}\right)_T}$$

Finally, using this result, we have:

$$\boldsymbol{\left(\frac{\partial P}{\partial T}\right)_V = n_{Avogadro}k\frac{1}{V}}$$

So that insertion into the relation above for internal energy:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{n_{Avogadro}k}{V} - \frac{n_{Avogadro}kT}{V} = 0$$

Demonstration of Exponential Temperature Dependencies of Diffusivity and the Rate Constant

Diffusivity and the chemical rate constant (k) show exponential increases with T. The partition function can be employed to quantify this phenomena, since the fraction of particles in the excited state – that fraction having sufficient energy to overcome an energy barrier – increase directly with temperature.

Most diffusional processes involve an excited state. If the average energy of an atom in a typical lattice is U_1, ΔU is the increase in energy for the atom to move from one site to another. If it is assumed that the quantized energy levels are so close together that a continuous curve may be used to describe the energy change, as shown in Figure HII.8.

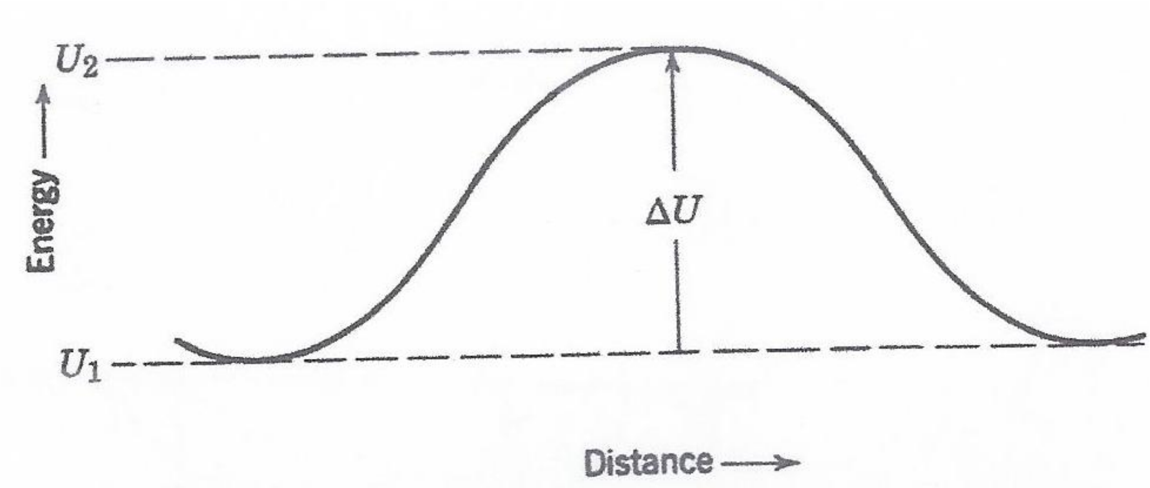


Figure HII.8 – Illustration of the activated state process as a continuous function.

The partition function $\wp$ may then be expressed as a continuum:

$$\boldsymbol{\wp = \sum_i \exp(-\epsilon_i/kT) = \int_0^\infty \exp(-U/kT)\, dU = kT}$$

For this calculation, not only those with energy $\boldsymbol{U_2}$ between $\boldsymbol{U_2 + dU}$ will be able to move over the barrier, but those with any high energy as well. The probability that an atom will have an energy between $\boldsymbol{U}$ and $\boldsymbol{U+ dU}$ is:

$$\boldsymbol{f(U)dU = \frac{\exp(-U/kT)dU}{\int_0^\infty \exp(-U/kT)\, dU}}$$

The probability that an atom will have an energy between $\boldsymbol{U_2}$ and $\boldsymbol{U = \infty}$ is:

$$\boldsymbol{f(U > U_2) = \int_{U_2}^\infty f(U)dU = \frac{\int_{U_2}^\infty \exp(-U/kT)dU}{\int_0^\infty \exp(-U/kT)\, dU}}$$

Or

$$\boldsymbol{f(U > U_2) = \exp(-U_2/kT)}$$

Similarly, the fraction of atoms having an energy between $\boldsymbol{U_1}$ and $\boldsymbol{U = \infty}$ is:

$$\boldsymbol{f(U > U_1) = \exp(-U_1/kT)}$$

Taking $\boldsymbol{U_1}$ as the ground state of the atom, then we have for the fraction of atoms in an excited state $\boldsymbol{f^*}$ corresponding to $\boldsymbol{U > U_2}$ (where ΔU is the activation energy) is:

$$\boldsymbol{f^* = \exp(-\Delta U/kT)}$$

This equation also describes the activation energy barrier necessary for atomic species to react in a chemical reaction.

This equation has to be refined further – it was assumed that the number of states available at any energy level is independent of the energy level. This is not categorically true, as entropy considerations need to be taken into account. So, this equation is modified into:

$$\boxed{\boldsymbol{f^{*} = \exp(\Delta S/kT)\exp(-\Delta U/kT)}}$$

In the above equation, $\boldsymbol{\Delta S}$ is the entropy change associated with the process. It clearly shows that the fraction of particles in a higher energy state increases exponentially with temperature as the activation energy level increases.

Distribution of Velocities in the Ideal Gas – the Maxwell-Boltzmann Versus the Fermi-Dirac Distribution

KTG was employed in HI to derive the average energy of an atom in a monatomic gas. However, this approach does not reveal any information on the distribution of velocities. This can now be derived employing the partition function. From Maxwell-Boltzmann, the final result (after a lengthy derivation) is:

$$\boxed{\boldsymbol{\langle v\rangle = \frac{\int_0^\infty vn(v)}{n} = \frac{8kT^{1/2}}{\pi m}}}$$

However, in the above derivation, the electron particles are not subject to the Pauli Exclusion Principle, which states that no two electrons may have the same set of quantum numbers, including electron spins.

So, the partition function is modified (again, after a lengthy derivation) to *subtract* from the quantized energy level $\boldsymbol{\epsilon_i}$ the Fermi energy $\boldsymbol{\epsilon_f}$. The two different distributions become equivalent when:

$$\boldsymbol{\exp\left(\frac{\varepsilon_i - \varepsilon_f}{kT}\right) \gg 1}$$

This is shown schematically in the following figure (HII.9).

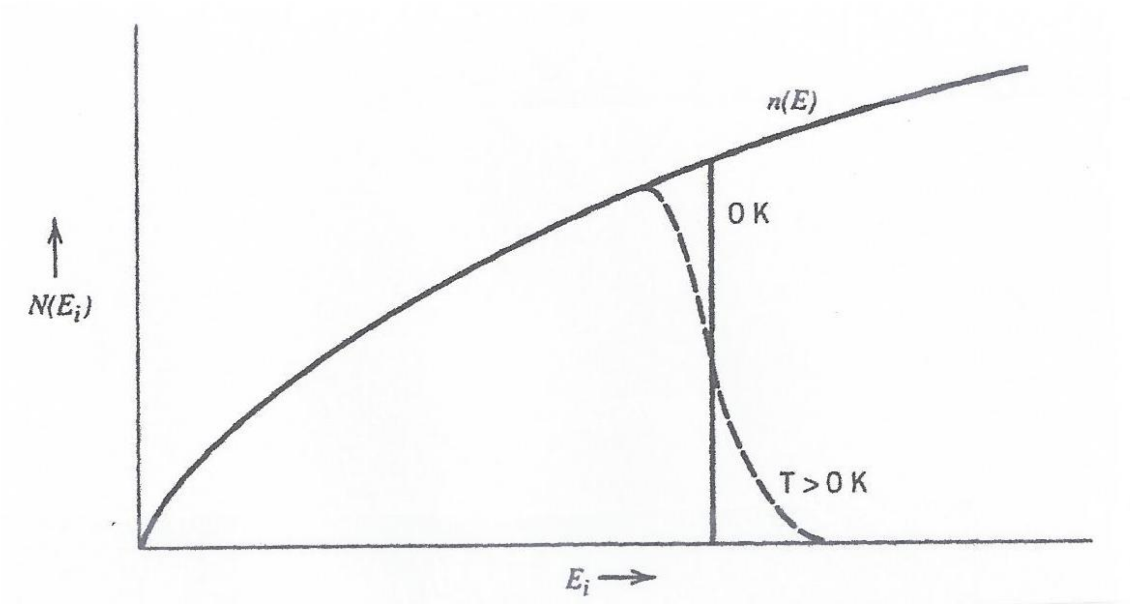


Figure HII.9 – The Fermi-Dirac distribution.

In contrast with the Maxwell-Boltzmann distribution, the population of states in the Fermi-Dirac distribution changes very little with temperature (i.e., only near the higher end of the distribution). This means with the latter distribution, it is necessary for only a few particles to change energy levels to change the temperature. This contrasts with the collection of the Maxwell-Boltzmann distribution, in which many more particles change energy levels to change temperature.

THEORETICAL CALCULATION OF HEAT CAPACITY

Background

Dulong and Petite (1819) postulated that all solid elements have a molar heat capacity equal to **3R** (2.4 J/°K) and Kopp (1865) postulated that the molar heat capacity of compound is the sum of that of its components. In accordance with Dulong and Petite, Figure HII.10 shows heat capacity to be highly non-linear in temperature, however, at room temperature most elements have heat capacities close to **3R**. Some elements, particularly silicon and the diamond structure for carbon show a lesser effect of temperature, and significantly lower values over a range of temperatures, especially at lower temperatures, as shown in Figure HII.10.

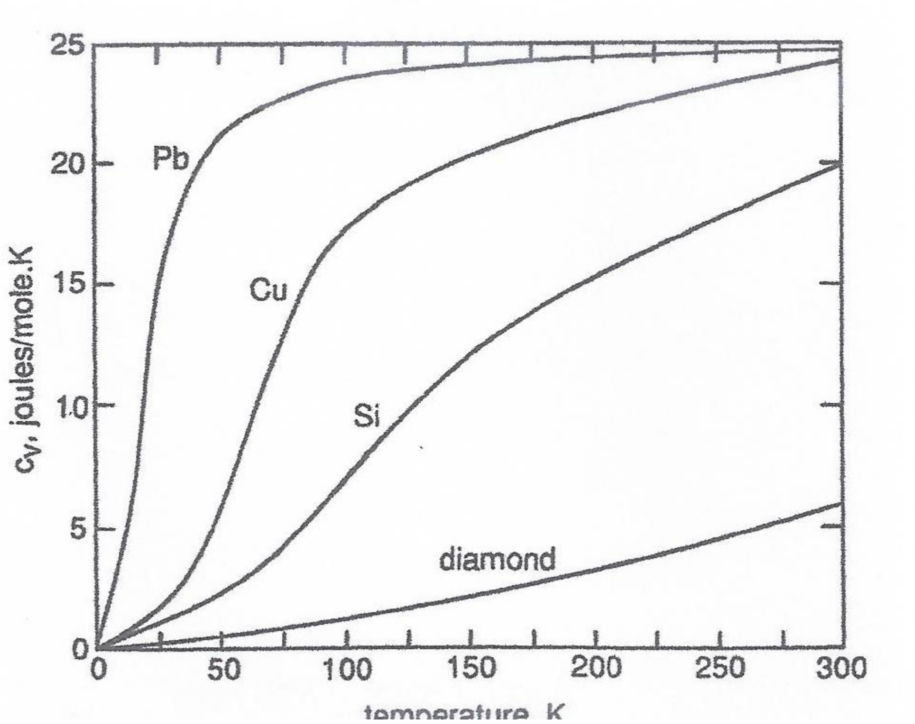


Figure HII.10 – The constant-volume molar heat capacities of Pb, Cu, Si, and the diamond form of C as a function of temperature.

With the advent, first of classical thermodynamics, then statistical thermodynamics, and finally, quantum theory, for the first time heat capacity was able to be calculated from first principles. Einstein (1907) was the first to have successfully made this calculation, using a simple mechanical analogue, where each of the $\boldsymbol{n}$ atoms of a crystal behave as a harmonic oscillator vibrating independently about its lattice point at a frequency of $\boldsymbol{\nu}$.

The Einstein Crystal

The energy of the ith level of a harmonic oscillator is given as:

$$\boldsymbol{\varepsilon_i = \{(i + 1/2)h\nu\}_{i=0,1,2,\ldots\infty}}$$

Considering the simplest treatment of vibration in all three directions, we have $\boldsymbol{3n}$ linear harmonic oscillators, and we have:

$$\boldsymbol{U' = 3\sum n_i \varepsilon_i}$$

Substitution of the equation for $\boldsymbol{\varepsilon_i}$ as a function of the vibration frequency and the partition function for $\boldsymbol{n_i}$ **(**$\boldsymbol{= nexp(-\epsilon_i/kT)/\wp}$**)** in this equation yields:

$$\boldsymbol{U' = 3\sum(i+1/2)h\nu\left\{\frac{n\cdot \mathbf{exp}(-(i+1/2)h\nu/kT)}{\sum \mathbf{exp}(-(i+1/2)h\nu/kT)}\right\} =}$$

$$\boldsymbol{3nh\nu\left\{\frac{\sum i\cdot \mathbf{exp}(-(i+1/2)h\nu/kT)}{\sum \mathbf{exp}(-(i+1/2)h\nu/kT)} + \frac{\frac{1}{2}\sum \mathbf{exp}(-(i+1/2)h\nu/kT)}{\sum \mathbf{exp}(-(i+1/2)h\nu/kT)}\right\} =}$$

$$\boldsymbol{3nh\nu\left\{\frac{\sum i\cdot \mathbf{exp}(-(i)h\nu/kT)}{\sum \mathbf{exp}(-(i)h\nu/kT)} + \frac{1}{2}\right\} =}$$

$$\boldsymbol{\frac{3}{2}nh\nu\left\{1 + \frac{2\sum i\cdot \mathbf{exp}(-(i)h\nu/kT)}{\sum \mathbf{exp}(-(i)h\nu/kT)}\right\}_{i=0,1,2,\ldots\infty} =}$$

Now, we can simplify this equation by replacing the series by its truncated bi-nomial series:

$$\boldsymbol{\frac{1}{(1-x)^2} = 1 + 2x + 3x^2 + \cdots \Rightarrow}$$

$$\boldsymbol{\frac{x}{(1-x)^2} = x + 2x^2 + 3x^3 + \cdots \Rightarrow}$$

Also, we have:

$$\frac{\mathbf{1}}{(\mathbf{1}-\boldsymbol{x})} = \mathbf{1} + \boldsymbol{x} + \boldsymbol{x}^{\mathbf{2}} + \cdots$$

First, we want to simplify our notation by setting $\boldsymbol{x} = \boldsymbol{exp}(-\boldsymbol{h\nu}/\boldsymbol{kT})$. So that

$$\sum \boldsymbol{i} \cdot \mathbf{exp}(-\boldsymbol{h\nu i}/\boldsymbol{kT}) \to \sum \boldsymbol{i}\boldsymbol{x}^{\boldsymbol{i}} = \mathbf{0}\boldsymbol{x}^{\mathbf{0}} + \mathbf{1}\boldsymbol{x}^{\mathbf{1}} + \mathbf{2}\boldsymbol{x}^{\mathbf{2}} + \mathbf{3}\boldsymbol{x}^{\mathbf{3}} + \cdots$$

But, since $\boldsymbol{x} + \mathbf{2}\boldsymbol{x}^{\mathbf{2}} + \mathbf{3}\boldsymbol{x}^{\mathbf{3}} + \cdots \approx \boldsymbol{x}/((\mathbf{1}-\boldsymbol{x})^{\mathbf{2}})$, then:

$$\sum \boldsymbol{i} \cdot \mathbf{exp}(-\boldsymbol{h\nu i}/\boldsymbol{kT}) = \frac{\mathbf{exp}(-\boldsymbol{h\nu i}/\boldsymbol{kT})}{\left(\mathbf{1} - \mathbf{exp}(-\boldsymbol{h\nu i}/\boldsymbol{kT})\right)^{\mathbf{2}}}$$

Finally, we have:

$$\mathbf{exp}(-\boldsymbol{h\nu i}/\boldsymbol{kT}) = \sum \boldsymbol{x}^{\boldsymbol{i}} = \mathbf{1} + \boldsymbol{z} + \boldsymbol{x}^{\mathbf{2}} + \cdots \cong \frac{\mathbf{1}}{(\mathbf{1}-\boldsymbol{x})}$$

Or

$$\frac{\mathbf{1} + \mathbf{2}\left(\frac{\boldsymbol{x}}{(\mathbf{1}-\boldsymbol{x})^{\mathbf{2}}}\right)}{\frac{\mathbf{1}}{(\mathbf{1}-\boldsymbol{x})}} = \mathbf{1} + \frac{\mathbf{2}\boldsymbol{x}}{(\mathbf{1}-\boldsymbol{x})}$$

Thus:

$$\boldsymbol{U}' = \frac{\mathbf{3}}{\mathbf{2}}\boldsymbol{nh\nu}\left(\mathbf{1} + \frac{\mathbf{2}\boldsymbol{x}}{(\mathbf{1}-\boldsymbol{x})}\right) =$$

$$\frac{\mathbf{3}}{\mathbf{2}}\boldsymbol{nh\nu}\left(\mathbf{1} + \frac{\mathbf{2exp}(-\boldsymbol{h\nu}/\boldsymbol{kT})}{\left(\mathbf{1} - \mathbf{exp}(-\boldsymbol{h\nu}/\boldsymbol{kT})\right)}\right)$$

Finally, we have:

$$\boldsymbol{U' = \frac{3}{2}nh\nu + \frac{3nh\nu}{\exp(h\nu/kT) - 1}}$$

So, we have:

$$\boldsymbol{c_V = \left(\frac{\partial U'}{\partial T}\right)_V = 3nh\nu(\exp(h\nu/kT) - 1)^{-2}\frac{h\nu}{T^2}\exp(h\nu/kT) =}$$

$$\boldsymbol{3nh\left(\frac{h\nu}{T}\right)^2 \frac{\exp(h\nu/kT)}{(\exp(h\nu/kT) - 1)^2}}$$

Letting $\boldsymbol{\Theta_E = h\nu/k}$, where $\boldsymbol{\Theta_E}$ is the Einstein Characteristic Temperature, and if we taken to be Avogadro's Number, we have for the *Einstein Crystal*:

$$\boxed{\boldsymbol{c_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\left(\frac{\theta_E}{T}\right) - 1\right)^2}}}$$

Figure HII.11 shows the variation of $\boldsymbol{c_V}$for Al with $\boldsymbol{\frac{T}{\theta_E}}$. Although the Einstein equation for $\boldsymbol{c_V}$ adequately represents the experimental values for heat capacity at higher temperatures ($\boldsymbol{\theta}$ taken as the adjustable parameter based on the data), this equation shows the theoretical values approach zero faster than the experimental values. This discrepancy is attributed to assuming only a single frequency for the harmonic oscillations.

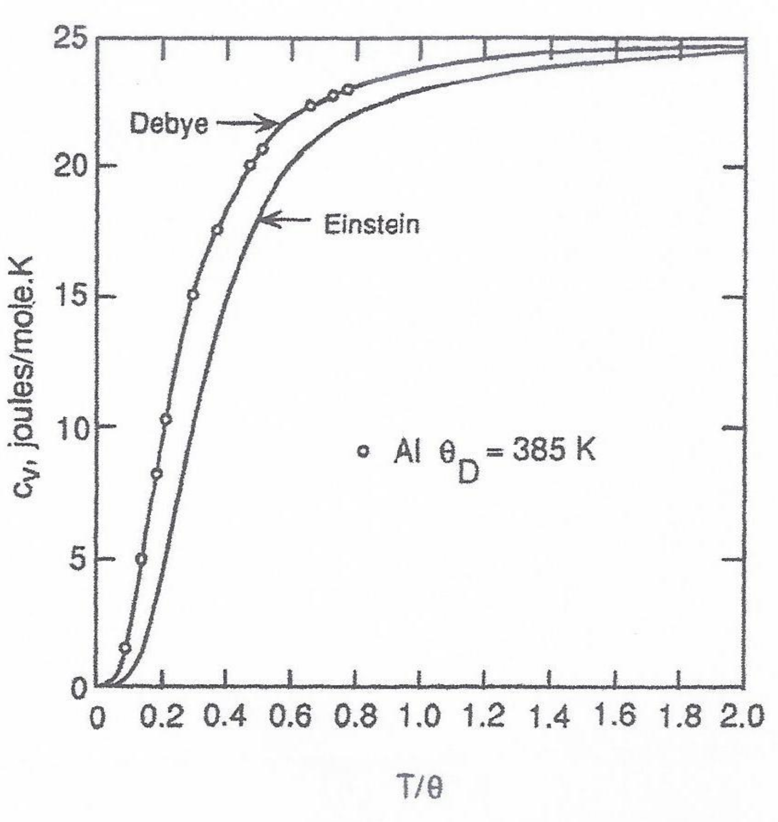


Figure HII.11- Variation of c_V for aluminum with $\boldsymbol{T/\Theta_E}$, where heat capacity is calculated by the Debeye equation, by the Einstein equation and measured.

Debeye (1912) devised a more complex model, by assuming a range of frequencies as is found in elastic vibration in a continuous solid. Taking the wavelength as equal to the inter-atomic distance, neighboring atoms would be in phase, so there would not be vibration of one atom with respect to another. In contrast, taking the shortest wavelength as twice the atomic distance, the neighboring atoms would vibrate in opposition to another.

- Taking $\boldsymbol{\lambda_{max}}$ to be on the order of 5 10^{-8} cm, the wave velocity would be 5 10^{5} cm/s, giving a maximum vibration of the atom as an oscillator about 10^{13}/s.

Debye assumed a frequency distribution, where the number of vibrations per unit volume per unit frequency range increase in a parabolic manner with increasing frequency in the allowed range of 0 to $\boldsymbol{\nu_{max}}$. By integrating Einstein's equation over this range of frequencies, Debye got:

$$\boldsymbol{C_V = \frac{9nh^3}{k^2\theta_D^3}\int_0^{\nu_D} \nu^2 \left(\frac{h\nu}{kT}\right)^2 \frac{\exp(h\nu/kT)}{(\exp(h\nu/kT)-1)^2}\, d\nu}$$

Taking $\boldsymbol{x = h\nu/k}$ gives:

$$\boldsymbol{C_V = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^{-x}}{(1-e^{-x})^2} dx}$$

In the above equation, ν_D is the maximum (Debeye) frequency, and $\boldsymbol{\Theta_D = h\nu_D \,/\, k}$ is the characteristic Debeye temperature of the solid. In a plot of $\boldsymbol{c_V}$ versus $\boldsymbol{log(T/\Theta_D)}$ (not shown) many of the data points to fall in a single line, verifying the advancement over the Einstein crystal, as shown in Figure HII.11.

The value of the integral from zero to infinity is 25.98, so that, at *very low temperatures*:

$$\boldsymbol{C_V = 9R25.98\left(\frac{T}{\theta_D}\right)^3 = 1943\left(\frac{T}{\theta_D}\right)^3}$$

The above equation is called the *Debeye T^3 Law* for heat capacity at low temperatures.

Debeye's theory does not consider the change of the energy of the electrons themselves with temperature. The electron theory of metals predicts the electronic contribution to the heat capacity is proportional to absolute temperature, so it becomes large at elevated temperatures.

Empirical Representation of Heat Capacities

The accepted analytical expression (whose constants are only applicable over the temperature range measured) is:

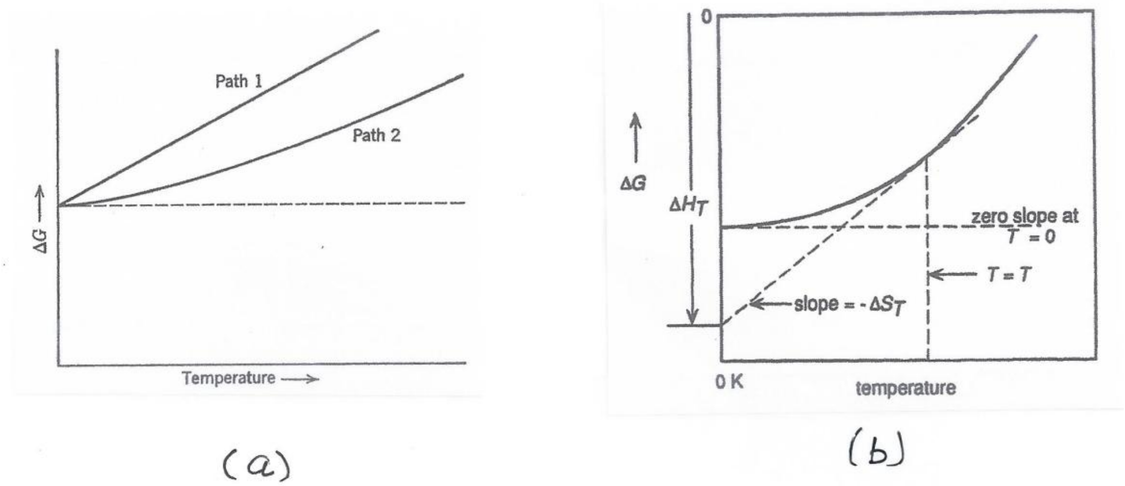
$$\boldsymbol{c_P = a + bT + cT^{-2}}$$

THE THIRD LAW (TL) OF THERMODYNAMICS

Background

With early attempts to understand the behavior of $\boldsymbol{\Delta G}$ with temperature as $\boldsymbol{T \rightarrow 0\ °K}$ by Le Chatelier in the latter half of the nineteenth century, and by Lewis in the early 20th century, a sounder understanding was finally achieved by Nernst in 1906 which was somewhat modified by Plank shortly after.

At issue is the slope of $\boldsymbol{\Delta G}$ with $\boldsymbol{T}$ (which is $\boldsymbol{\Delta S}$) near absolute zero. Figure HII.12 shows two possible paths, whether the slope is essentially constant, or whether the slope goes to zero.



(a) (b)

Figure HII.12 – (a) Two possible ways for $\Delta \boldsymbol{G}$ to approach $\Delta \boldsymbol{H}$ near 0 °K: Path *1*$\Delta \boldsymbol{S} \neq \mathbf{0}\ \boldsymbol{as}\ \boldsymbol{T} \rightarrow \mathbf{0}$ and Path *2* $\Delta \boldsymbol{S} \rightarrow \mathbf{0}\ \boldsymbol{as}\ \boldsymbol{T} \rightarrow \mathbf{0}$. (b) Variation of the change in the Gibbs Free Energy for a reaction with temperature approaches absolute zero.

Nernst postulated a *heat theorem* that states: *for all reactions involving substances in the condensed state,* $\boldsymbol{\Delta S} = \mathbf{0}$ *at* $0\ °K$. Plank added: *the entropy of any homogeneous substance, which is in complete internal equilibrium, may be taken as zero at absolute zero*.

A more contemporary statement is (A. Sommerfell, 1956): *As the temperature of a system tends to zero at absolute temperature, its entropy tends to a constant value ,* *which is independent of pressure, state of aggregation, etc*.

What does this really mean?

- For a given process $\boldsymbol{\Delta S} = \mathbf{0}$ *at* $0\ °K$. If a given system consists of two or more substances, only their differences in entropy are zero, but the entropies of the individual substances themselves $\boldsymbol{S}_{\boldsymbol{i},\mathbf{0}}$ need not be zero.
- Since $\boldsymbol{S}_{\boldsymbol{i},\mathbf{0}}$ need not be zero itself, and since it is un-measureable, by convention, the *absolute* values for the entropy of the individual components of a reaction in the same standard state are assigned a value of zero as a reference state:

$$\boldsymbol{S_T = \int_0^T \frac{C_P}{T} dT + S_0 = \int_0^T \frac{C_P}{T} dT}$$

Plank's and Nernst's original theorem applied to only pure, crystalline solids, not to solutions, or glasses, and it later turned out to be applicable to gases and pure compounds, as well as substances in different standard states (i.e., different crystal structures). Situations where there is not complete internal equilibrium typically involve a lack of energy or time for complete ordering into the lowest energy state to occur. Examples are:

1. *Solid solution* – As a stable solid solution is cooled to absolute zero, two processes may occur:
    a. The maximum solubility of one of the constituents in a crystal decreases all the way to zero at absolute zero, in which case, the solute has completely precipitated out;
    b. The solid solution becomes ordered with respect to arrangement of the constituents on the lattice.

    If either one of these two processes were to occur completely, $\boldsymbol{S = 0}$, but, in reality, as temperature decreases, there could be a lack of mobility and a *metastable* structure could be frozen in, in which the ordered state is not one of the lowest energy, or some randomness is frozen in.

2. *Pure Crystalline Solid With Vacancies* - At a finite temperature, a pure crystalline solid solution contains an equilibrium number of vacant lattice sties (due to random positioning, resulting in an entropy of mixing).

3. *Compounds not Completely Ordered* – Similarly to the problem of vacancies remaining as $\boldsymbol{T \to 0\ {}^\circ K}$, a compound may not have sufficient mobility to be completely ordered, including crystallographic disorientation. In principle, a completely ordered compound has a zero entropy, as discussed previously.

4. *Glasses* – This class of materials is essentially a super-cooled liquid, where the ordering is short ranged. It obviously does not exhibit internal equilibrium, as even at temperatures well above absolute zero, a high degree of atomic disorder is the case, with immobility preventing a unique freezing temperature in a reasonable time. This is observed macroscopically as a viscous liquid.

<u>Effect of Temperature on Entropy, and Its Consequences</u>

Starting with the definition $\boldsymbol{\Delta G = \Delta H - T\Delta S}$, we can take the total differential:

$$\boldsymbol{d\Delta G = d\Delta H - Td\Delta S - \Delta S dT}$$

This equation becomes, on rearrangement at constant pressure:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P - T\left(\frac{\partial \Delta S}{\partial T}\right)_P - \Delta S =$$

$$\Delta C_P - T\left(\frac{\partial \Delta S}{\partial T}\right)_P - \Delta S$$

Also, we have: $dG = -SdT + VdP$, which can be restated as:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

Thus:

$$\Delta C_P = T\left(\frac{\partial \Delta S}{\partial T}\right)_P$$

As $T \to 0\ °K$, $\Delta c_P \to 0\ °K$ if $(\partial \Delta S/\partial T)$ is finite as $T \to 0\ °K$.

Effect of Pressure on Enthalpy and Entropy

For a closed system of fixed composition undergoing a change of pressure at constant temperature:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP$$

And, since we have $dH = TdS + VdP$, then:

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

From Maxwell, we have the following equivalency:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Thus, we have:

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

We also have the isobaric coefficient of thermal expansion α:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Thus, we have:

$$\left(\frac{\partial H}{\partial P}\right)_T = \alpha V + V = V(1 - \alpha T)$$

Finally, the change in molar enthalpy from State 1 (***P_1*, *T***) to State 2 (***P_2*, *T***) is:

$$\Delta H = H(P_2, T) - H(P_1, T) = \int_{P_1}^{P_2} V(1 - \alpha T)dP$$

For the effect of temperature and pressure on entropy, we begin with the effect of temperature for a given pressure:

$$\Delta \boldsymbol{S} = \boldsymbol{S}(\boldsymbol{T_2}, \boldsymbol{P}) - \boldsymbol{S}(\boldsymbol{T_1}, \boldsymbol{P}) = \int_{T_1}^{T_2} \frac{\boldsymbol{C_P}}{\boldsymbol{T}} \boldsymbol{dT}$$

For the effect of pressure:

$$\boldsymbol{dS} = \left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{P}}\right)_{\boldsymbol{T}} \boldsymbol{dP}$$

But, we have from Maxwell:

$$\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{P}}\right)_{\boldsymbol{T}} = -\boldsymbol{\alpha V}$$

Thus, we have:

$$\Delta \boldsymbol{S} = \boldsymbol{S}(\boldsymbol{P_2}, \boldsymbol{T}) - \boldsymbol{S}(\boldsymbol{P_1}, \boldsymbol{T}) = \int_{P_1}^{P_2} -\boldsymbol{\alpha V dP}$$

For an ideal gas, this is:

$$\Delta \boldsymbol{S} = \int_{P_1}^{P_2} -\boldsymbol{R d} \ln \boldsymbol{P} = -\boldsymbol{R} \ln \frac{\boldsymbol{P_2}}{\boldsymbol{P_1}}$$

Finally for the effects of both temperature and pressure on entropy, we have:

$$\Delta \boldsymbol{S} = \boldsymbol{S}(\boldsymbol{P_2}, \boldsymbol{T_2}) - \boldsymbol{S}(\boldsymbol{P_1}, \boldsymbol{T_1}) = \int_{T_1}^{T_2} \frac{\boldsymbol{C_P}}{\boldsymbol{T}} \boldsymbol{dT} + \int_{P_1}^{P_2} -\boldsymbol{\alpha V dP}.$$

THE ENTHALPY BALANCE

Enthalpy as a Function of Temperature: Chemical Reactions and Phase Change

For a closed system of fixed composition undergoing a change in temperature from T_1 to T_2 at constant P, we have:

$$\Delta H = H(T_2, P) - H(T_1, P) = \int_{P_1}^{P_2} c_P dT$$

From this equation, it can be seen that, graphically, ΔH_{rxn} is simply the area under the curve of $c_P$versus T between the limits T_1 and T_2, where c_P is generally a function of T**.**

When a system undergoes a chemical reaction, or a transformation, the change in enthalpy is the difference between the enthalpy of the products (State 2) and the enthalpy of the reactants (State 1): viz.:

Chemical Reaction: $A + B \overset{T,P}{\leftrightarrow} AB \qquad \Delta H_{rxn} = ?$

Phase Change: $A^{\alpha} \overset{T,P}{\leftrightarrow} A^{\beta} \qquad \Delta H^{\alpha \to \beta} = ?$

$$\Delta H_{rxn}(T, P) = H_{AB}(T, P) - \{H_A(T, P) + H_B(T, P)\}$$

$$\Delta H^{\alpha \to \beta}(T, P) = H^{\beta}(T, P) - H^{\alpha}(T, P)$$

This is known as *Hess'Law*. As $\Delta H_{T,P} = Q$, if ΔH *is negative*, heat is evolved by the system, and the reaction is considered to be *exothermic*. Likewise, if ΔH *is positive*, heat is absorbed from the surroundings, and the process is *endothermic*.

To determine ΔH for a process change, such as a chemical reaction or a phase change for any T at constant P, the enthalpy change for all species (reactants and products) is calculated, and an enthalpy balance (i.e., cycle) calculation is made given ΔH from a given temperature. This procedure is known as *Kirkhoff's Law, or Kirkhoff's Square*. This procedure is illustrated in Figure HII.13 for the case of melting.

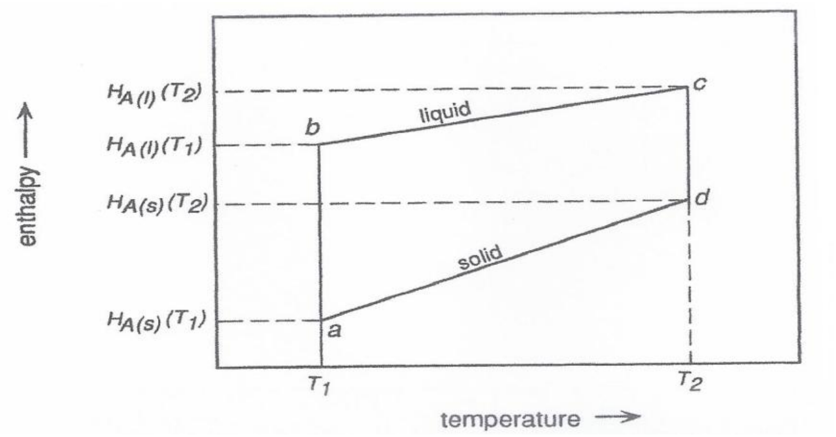


Figure HII.13 – Illustration of Kirckhoff's Square.

Consider the phase change for Species A:

At T_1: $A^S \overset{T,P}{\leftrightarrow} A^L \qquad \Delta H_{T_1}^{L-S} = H_{T_1}^L - H_{T_1}^S = ?$

At T_2: $A^S \overset{T,P}{\leftrightarrow} A^L \qquad \Delta H_{T_2}^{L-S} = H_{T_2}^L - H_{T_2}^S = ?$

Not surprisingly, as enthalpy is a state property, the enthalpy change at one temperature can be calculated given the enthalpy change at another temperature if the heat capacities of the liquid and solid are known. This is shown by the following enthalpy balance:

$$\Delta H(a \to b) = \Delta H(a \to d) + \Delta H(c \to d) + \Delta H(c \to b)$$

$$\Delta H(a \to d) = \int_{T_1}^{T_2} c_P^S dT$$

$$\Delta H(d \to c) = \Delta H_{T_2}^{L-S}$$

$$\Delta H(c \to b) = \int_{T_2}^{T_1} c_P^L dT = -\int_{T_1}^{T_2} c_P^L dT$$

So, for Species A, we have:

$$\Delta H_{T_1}^{L-S} = \Delta H_{T_2}^{L-S} + \int_{T_1}^{T_2} c_P^S dT - \int_{T_1}^{T_2} c_P^L dT$$

Thus, we have, generally:

$$\Delta \boldsymbol{H}_{\boldsymbol{T_2}} = \Delta \boldsymbol{H}_{\boldsymbol{T_1}} + \int_{\boldsymbol{T_1}}^{\boldsymbol{T_2}} \Delta \boldsymbol{c_P} \boldsymbol{dT}$$

In the above equation $\Delta \boldsymbol{c_P} = \boldsymbol{c_P^L} - \boldsymbol{c_P^S}$.

Clearly, one of the two enthalpies for the phase change must be known, as well as the heat capacities of the species in both states. If $\Delta \boldsymbol{c_P} \approx \boldsymbol{0}$, then $\Delta \boldsymbol{H}$ can be considered to be independent of temperature. (True for small enough changes in temperature for any species, and surprisingly true for many species when the experimental error is taken into account, allowing the same heat capacities to be employed at process temperature versus, say, room temperature; a better shortcut is to take an average of a heat capacity over a temperature range, then, use this average as if it were a constant.)

As enthalpy does not have an absolute value (either does entropy) only changes in enthalpy $\Delta \boldsymbol{H}$ can be measured. For facility in use, by convention, the enthalpy of any element in its stable state at 298° K (25° C) is assigned a value of zero enthalpy. This is not true for the enthalpy change for a reaction or a phase change, in which case, they must be measured. These are tabulated for 298° K (25° C). This is stated symbolically for the oxide *MO* as follows:

$$\boldsymbol{M(s)} + \frac{\boldsymbol{1}}{\boldsymbol{2}} \boldsymbol{O_2(g)} = \boldsymbol{MO(solid)}$$

$$\Delta \boldsymbol{H}_{\boldsymbol{298}}^{\boldsymbol{MO}} = \boldsymbol{H}_{\boldsymbol{MO(s),298}} - \boldsymbol{H}_{\boldsymbol{M(s),298}} - \frac{\boldsymbol{1}}{\boldsymbol{2}} \boldsymbol{H}_{\boldsymbol{O_2,298}}$$

When there are phase changes, including melting among either the elements or compounds, or both, the foregoing procedure still applies, but proper accounting of signs and standard states can be cumbersome.

This procedure for a complex reaction involving both elements and compounds can be generalized. Consider the cycle shown in Figure HII.14.

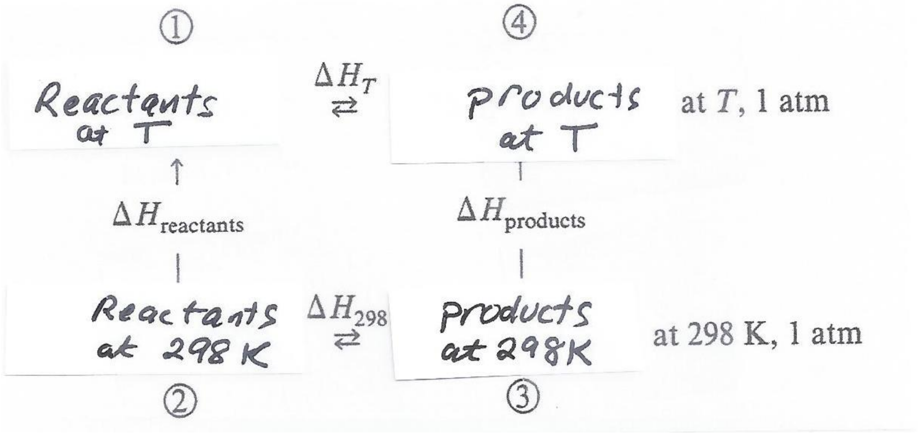


Figure HII.14 – Illustration of application of the Kirkhoff Square to a generalized chemical reaction.

The general procedure can be stated as:

$$\boxed{\begin{aligned}\Delta \boldsymbol{H}_{\boldsymbol{T}}^{\boldsymbol{rxn}} - \Delta \boldsymbol{H}_{\boldsymbol{298}}^{\boldsymbol{rxn}} \\ &= \Delta \boldsymbol{H}_{\boldsymbol{298\to T}}^{\boldsymbol{products}} - \Delta \boldsymbol{H}_{\boldsymbol{298\to T}}^{\boldsymbol{reactants}} + \sum \Delta\, \boldsymbol{H}^{\boldsymbol{products}\ \boldsymbol{\alpha_i\to\beta_i}} \\ &\quad - \sum \Delta\, \boldsymbol{H}^{\boldsymbol{reactants}\ \boldsymbol{\alpha_i\to\beta_i}}\end{aligned}}$$

The enthalpy change $\Delta \boldsymbol{H}_{\boldsymbol{298}}^{\boldsymbol{reactants}}$ is for any compound appearing as a reactant, and is found in a table. Likewise $\Delta \boldsymbol{H}_{\boldsymbol{298}}^{\boldsymbol{products}}$ is for any compound appearing as a product.

The enthalpy change for $\Delta \boldsymbol{H}_{\boldsymbol{298\to T}}$ is the overall integral $\int_{298}^{T} \boldsymbol{c_P}$ (for products and for reactants). Care must be taken to employ the value for $\boldsymbol{c_P}$ only over the temperature for which it is valid for each state. Thus, there can be intermediate temperatures where a change of phase occurs that necessitates employing a different value for $\boldsymbol{c_P}$ in the integration over the temperature range and state for which it is valid.

As a result, there can be multiple integrals, each over a different temperature range within the over temperature change of 298 to $\boldsymbol{T}$**,** each temperature range associated with a specific $\boldsymbol{c_P}$ for the state valid over that temperature range. Also, as $\Delta \boldsymbol{H}$ is per mole, the stoiciometry of the reaction as written has to be taken into account.

Finally $\sum \Delta \boldsymbol{H}^{\boldsymbol{\alpha_i\to\beta_i}}$ refers to the sum of all the enthalpy changes from phase changes a (for the reactants, separately for the products) such as from changes in crystal structure and change of state, such as melting. There can be multiple contributions due to several possible changes in crystal structure (both elements as well as compounds) before melting.

Example of a Complex Reaction and Associated Enthalpy Balance

As a relatively simple example, consider the reaction at 1 atm:

$$\boldsymbol{4Al + 3SiO_2 \overset{\Delta H_T}{\Longleftrightarrow} 3\mathrm{Si}{+}2\mathrm{A}l_2O_3}$$

Figure HII.14 shows the Kirkhoff Square qualitatively for this reaction.

$$\begin{tikzcd}
① & & ④ & \\
4\mathrm{Al} + 3\mathrm{SiO}_2 \arrow[rr, shift left, "\Delta H_T"] & & 3\mathrm{Si} + 2\mathrm{Al}_2\mathrm{O}_3 \arrow[ll, shift left] & \text{at } T\text{, 1 atm} \\
4\mathrm{Al} + 3\mathrm{SiO}_2 \arrow[u, "\Delta H_{\text{reactants}}"] \arrow[rr, shift left, "\Delta H_{298}"] & & 3\mathrm{Si} + 2\mathrm{Al}_2\mathrm{O}_3 \arrow[ll, shift left] \arrow[u, "\Delta H_{\text{products}}"] & \text{at 298 K, 1 atm} \\
② & & ③ &
\end{tikzcd}$$

Figure HII.15 – The Kirckhoff Square for reduction of quartz (SiO_2) with aluminum.

We want to evaluate $\boldsymbol{\Delta H^{rxn}}$ for this reaction at 800 °C (1073 °K). However, we must consider the fact that quartz transforms from the form to the form at 848 °C, with an enthalpy change: $\boldsymbol{\Delta H_{SiO_2}^{\alpha\to\beta} = 150\,\frac{cal}{mole}}$. Also, Al melts at 932 °K, with: $\boldsymbol{\Delta H_{Al}^{S\to L} = 2500\,\frac{cal}{mole}}$. Thus for our general equation, we have:

$$\boldsymbol{\Delta H_{298} = 2\Delta H^{o}{}_{298,Al_2O_3} - 3\Delta H^{o}{}_{298,\alpha-quartz}}$$

$$\boldsymbol{= 2(-400,000) - 3(-217,000) =}$$

$$\boldsymbol{-149,000\ \mathrm{cal}}$$

And, we have for the phase changes:

$$\sum \Delta \boldsymbol{H}^{\boldsymbol{products}\,\boldsymbol{\alpha_i\to\beta_i}} = \mathbf{0}$$

But

$$\sum \Delta \boldsymbol{H}^{\boldsymbol{reactants}\,\boldsymbol{\alpha_i\to\beta_i}} = \mathbf{3}\Delta\boldsymbol{H}^{\,\boldsymbol{\alpha\to\beta}} + \mathbf{4}\Delta\boldsymbol{H}_{\boldsymbol{Al}}^{\boldsymbol{l\to s}} =$$

$$-\mathbf{3}(\mathbf{150}) - \mathbf{4}(\mathbf{2500})$$

Finally, we need to evaluate:

$$\Delta\boldsymbol{H}_{\mathbf{298}\to\boldsymbol{T}}^{\boldsymbol{products}} - \Delta\boldsymbol{H}_{\mathbf{298}\to\boldsymbol{T}}^{\boldsymbol{reactors}} = \int_{\mathbf{298}}^{\boldsymbol{T}=\mathbf{1073}} \Delta\boldsymbol{c_P}\boldsymbol{dT}$$

For the above equation, it is noted that $\boldsymbol{c_P}$ is different, depending on the crystal structure:

$$\int_{\mathbf{298}}^{\boldsymbol{T}=\mathbf{1073}} \Delta\boldsymbol{c_P}\boldsymbol{dT}$$

$$= \int_{\mathbf{298}}^{\mathbf{848}} \{\mathbf{2}\boldsymbol{c_P}(\boldsymbol{Al_2O_3}, \boldsymbol{s}) + \mathbf{3}\boldsymbol{c_P}(\boldsymbol{Si}, \boldsymbol{s}) - \mathbf{4}\boldsymbol{c_P}(\boldsymbol{Al}, \boldsymbol{s}) - \mathbf{3}\boldsymbol{c_P}(\boldsymbol{\alpha}\ \boldsymbol{quartz}\}\boldsymbol{dT}$$
$$+$$

$$\int_{\mathbf{848}}^{\mathbf{932}} \{\mathbf{2}\boldsymbol{c_P}(\boldsymbol{Al_2O_3}, \boldsymbol{s}) + \mathbf{3}\boldsymbol{c_P}(\boldsymbol{Si}, \boldsymbol{s}) - \mathbf{4}\boldsymbol{c_P}(\boldsymbol{Al}, \boldsymbol{s}) - \mathbf{3}\boldsymbol{c_P}(\boldsymbol{\beta}\ \boldsymbol{quartz}\}\boldsymbol{dT} +$$

$$\int_{\mathbf{932}}^{\mathbf{1073}} \{\mathbf{2}\boldsymbol{c_P}(\boldsymbol{Al_2O_3}, \boldsymbol{s}) + \mathbf{3}\boldsymbol{c_P}(\boldsymbol{Si}, \boldsymbol{s}) - \mathbf{4}\boldsymbol{c_P}(\boldsymbol{Al}, \boldsymbol{l}) - \mathbf{3}\boldsymbol{c_P}(\boldsymbol{\beta}\ \boldsymbol{quartz}\}\boldsymbol{dT} +$$

$$-\mathbf{3}(\mathbf{150}) - \mathbf{4}(\mathbf{2500})$$

A more complex reaction might involve phase changes and melting of both elements and compounds in both the reactants and products.

Application of the Enthalpy Balance – The Process Heat Balance

The enthalpy balance (when combined with a mass balance for an open system) is central to understanding and modeling materials processes – whether they are examined on a fundamental level, or whether they are of the scale and scope of an industrial process. It provides a framework for more sophisticated modeling incorporating, for example, rate laws. Typically heat losses have to be considered, and often there are mass flows to consider.

Here, we are going to consider a very simple system that is closed and adiabatic, with no exchange of mass or heat with its surroundings. The enthalpy balance is shown to determine what fraction of a pure metal will freeze when super-cooled below its equilibrium freezing point.

Consider a quantity of liquid tin that is super-cooled 10 °K below its equilibrium melting point of 505 °K. It is adiabatically contained. After nucleation (at 495° K) the tin freezes spontaneously. What is the fraction of tin that is able to freeze?

The data needed for this problem is as follows:

$$\boldsymbol{\Delta H_{505}^{l\to s} = -1690\,\frac{\mathbf{cal}}{\mathbf{mole}}\,@\,505\,°\mathrm{K}}$$

$$\boldsymbol{\Delta c_P^{Sn,l} = 8.29 - 2.2\;10^{-3}\,\frac{\mathbf{cal}}{\mathbf{mole}}\,°\mathrm{K}}$$

$$\boldsymbol{\Delta c_P^{Sn,s} = 4.42 - 6.3\;10^{-3}\,\frac{\mathbf{cal}}{\mathbf{mole}}\,°\mathrm{K}}$$

$$\boldsymbol{T_{Sn}^{mp} = 505\,°\mathrm{K}}$$

The equilibrium state is the co-existence of liquid and solid tin at the melting point. The fraction of tin able to solidify depends in this case only on the quantity of heat that brings the system back to its melting point, but no higher.(Thus, different metals, each with different heats of freezing, different melting points and different heat capacities, will result in different fractions for an equivalent degree of super-cooling. Also, in point of fact, this degree of super-cooling itself, can be a variable, depending on nucleation factors intrinsic to the metal at issue.) Since the system is adiabatic, there are no heat losses to take into account. (If, for example, this process were to occur in a mold, the heat losses to the mold, depending on heat transfer issues, would need to be taken into account.)

As enthalpy is a state property, the process path is immaterial. Here, we can consider one of two paths shown in the figure below (HII.16). It is immaterial which path to choose, because the enthalpy balance is closed, so either path gives the same answer.

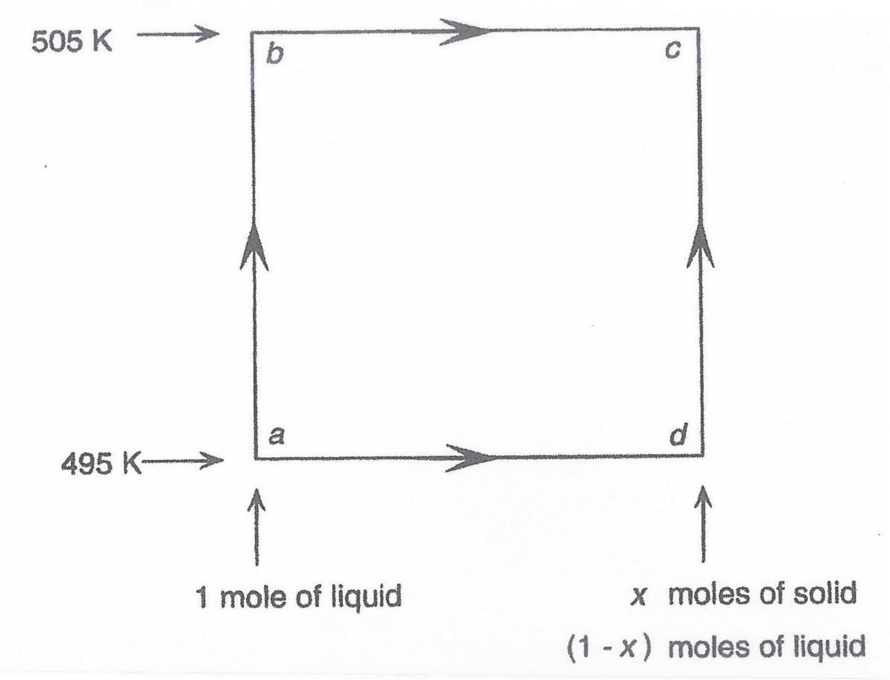


Figure HII.16 – Enthalpy balance for the spontaneous freezing of super-cooled tin, showing two possible thermodynamic paths: *a*→*b*→*c*, or *a*→*d*→*c*.

Taking Path *a*→*b*→*c* , we have the following enthalpy balance:

$$\Delta \boldsymbol{H}_{(\boldsymbol{a}\to\boldsymbol{b})} + \Delta \boldsymbol{H}_{(\boldsymbol{b}\to\boldsymbol{c})} = \mathbf{0}$$

$$\Delta \boldsymbol{H}_{(\boldsymbol{a}\to\boldsymbol{b})} = \int_{495}^{505} \boldsymbol{c}_{\boldsymbol{P}}^{\boldsymbol{l}}\, \boldsymbol{dT} = \mathbf{8.29 \cdot 10} - \frac{\mathbf{2.2}}{\mathbf{2}} \mathbf{10^{-3}(505^2 - 495^2) = 71.9\ cal}$$

$$\Delta \boldsymbol{H}_{(\boldsymbol{b}\to\boldsymbol{c})} = \mathbf{-1690}\boldsymbol{x}$$

Solving the above leads to:

$$\boldsymbol{x = \frac{71.9}{1690} = 0.0425}$$

The above result indicates that only about 4% of the tin can solidify!

Alternatively, for Path *a→d→c*, we can write an enthalpy balance – note that this path is irreversible, but can be used to evaluate the change in enthalpy:

$$\boldsymbol{\Delta H_{(a\to d)} + \Delta H_{(d\to c)} = 0}$$

$$\boldsymbol{\Delta H_{(a\to d)} = -x\Delta H_{495}^{l\to s}}$$

$$\boldsymbol{\Delta H_{(d\to c)} = x\left\{\int_{495}^{505} c_P^s dT\right\} + (1-x)\left\{\int_{495}^{505} c_P^l dT\right\} = 71.9 + 3.8x}$$

But, we also have:

$$\boldsymbol{\Delta H_{495}^{l\to s} = \Delta H_{505}^{l\to s} + \int_{505}^{495} \Delta c_P^{s\to l} dT =}$$

$$\textbf{1694 cal/mole}$$

Solving the above equation leads to:

$$\boldsymbol{-1694x = -3.8x - 71.9 \Rightarrow}$$

$$\boldsymbol{x = 0.0425}$$

Obviously, the first path (*a→b→c*) is easier to evaluate, because the data as given for the enthalpy change on melting is employed directly. The actual path taken – which will be irreversible – will be between these two extreme possible paths, because the process of freezing *and* the increase in temperature occur simultaneously!