Conditions for Stable Equilibrium

- Consider the conditions for spontaneity:
  - Isolated system

$$dS_{sys} > 0$$

  - Nonisolated system

$$dS_{tot} = dS_{sys} + dS_{surr} > 0$$

  or

$$dS_{sys} > -dS_{surr}$$

  or

$$dS_{sys} > \frac{dq_{rev}}{T_{surr}}$$

- Since $dq = dU - dw$

$$dS_{sys} > \frac{dU_{sys}}{T_{surr}} + \frac{P_{ext}\ dV}{T_{surr}}$$

  (This assumes that only pressure-volume work is involved.)

- Rewriting:

$$T_{surr} dS > dU + P_{ext} dV$$

  gives an expression for a system moving spontaneously to a new equilibrium.

  - Note that anything without a subscript applies to the system.

- If the system is at equilibrium then $T_{surr} = T$ and $P_{ext} = P$ and the equation becomes:

$$TdS = dU + PdV$$

  which is the Master Equation.

- Different constraints (or different ways of being in contact with the surroundings) give rise to different conditions for equilibrium.
- Consider the case of constant volume and constant entropy:

$$dV = 0; dS = 0$$

  Then:

$$dS_{sys} > \frac{dU_{sys}}{T_{surr}} + \frac{P_{ext}\ dV}{T_{surr}}$$

  becomes:

$$0 > dU_{V,S}$$

  or

$$dU_{V,S} < 0$$

- Consider another (different) case where U and V are constant.

$$dU = 0; dV = 0$$

  - Then the condition for spontaneous change becomes:

$$dS_{U,V} > 0$$

- The constraints of constant entropy and volume correspond to those of:
    - a closed isolated system.
    - a system undergoing an adiabatic reversible process at constant volume.
- Systems of chemical interest are couple to their surroundings by one of the following:
    - external forces (pressure or external field).
    - thermal contact (constant T reservoir)
    - material contact (such that the system exchanges matter with the surroundings)
    - reactive contact (in which an exchange of matter influences chemical reactions withing the system).
- Now consider enthalpy:

  $$H \equiv U + PV$$

  or in differential form:

  $$dH = dU + d(PV) = dU + PdV + VdP$$

  or

  $$dU = dH - PdV - VdP$$

    - Substituting into the condition for spontaneity:

      $$T_{surr}dS > dH - PdV - VdP + P_{ext}dV$$

    - Under the constraints of constant P and S, $dP = 0$, $dS = 0$ and $P_{ext} = P$, the condition for spontaneity becomes:

      $$dH_{P,S} < 0$$

      and the enthalpy decreases as much as possible during the process.
- What about other constraints, such as $dV = 0, dT = 0$ or $dP = 0, dT = 0$?
    - We need to have thermodynamic functions which include entropy and have (V, T) or (P, T) as their natural variables.
    - Also the thermodynamic function should decrease during the spontaneous process.

Helmholtz Free Energy, A

- Consider first constant T and V.
- Define $A = U - TS$.
    - Then:

      $$dA = dU - SdT - TdS$$

      or

      $$dU = dA + SdT + TdS$$

- Thus the condition for spontaneity becomes:

  $$T_{surr}dS > dA + TdS + SdT + P_{ext}dV$$

- Applying the conditions of constant T ($dT = 0$ and $T_{surr} = T$) and constant V ($dV = 0$) yields:

  $$0 > dA_{T,V}$$

Gibbs Free Energy, G

- Consider constant T and P.
- Define $G = H - TS$.
  - Then

$$dG = dH - SdT - TdS$$

or

$$dG = dU + PdV + VdP - SdT - TdS$$

or

$$dU = dG - PdV - VdP + SdT + TdS$$

- Thus the condition for spontaneity becomes:

$$T_{surr}dS > dG - PdV - VdP + TdS + SdT + P_{ext}dV$$

- Applying the conditions of constant T ($dT = 0$ and $T_{surr} = T$) and constant P ($P = P_{ext}$, $dP = 0$) yields:

$$0 > dG_{T,P}$$

- In summary, the condition for spontaneity is that entropy is maximized and under various constraints, this becomes:

$$dU_{V,S} < 0$$

$$dH_{P,S} < 0$$

$$dA_{T,V} < 0$$

$$dG_{T,P} < 0$$

Legendre Transforms

- U, H, A, and G are thermodynamic potential energy functions and are Legendre Transforms of each other.
- S and T are a pair of conjugate variables.
- P and V are pair of conjugate variables.
- Start with the Master Equation:

$$dU = TdS - PdV$$

  - Each of the other thermodynamic potentials is a transform of one of the others:

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS$$

  - Each transformation involves the addition or subtraction of a pair of conjugate variables.
- Spontaneous processes minimize potential.

A Closer Look at Stability

- Recall the case of two identical metal cubes (a and b) at different temperatures which are allowed to equilibrate under the constraints of constant U and P.
- Change the constraints to constant S and P.
- Does a new spontaneous process occur?
- Use a engine to transfer energy form one cube to another (Figure 5.1).
  - Energy can be transferred as heat or as adiabatic work.
  - Energy can be transferred to or from the surroundings.
  - The constraint of constant S means that $S_a + S_b$ is constant.
- Allow the temperatures of the cubes to change, but keep the volumes of the cubes constant.
- What is $dH_{S,P}$?
  - If $dH_{S,P} < 0$, then a spontaneous process will occur as a result of changing the constraints from $dU = 0; dP = 0$ to $dS = 0; dP = 0$.
  - If $dH_{S,P} = 0$, then the system is at equilibrium under the new constraints. Equilibrium under the new constraints requires no work.
  - If $dH_{S,P} > 0$, then the system is stable under the new constraints and no spontaneous process may occur.
- If S is constant then

$$0 = dS = dS_a + dS_b = \frac{C_P}{T_a} dT_a + \frac{C_P}{T_b} dT_b$$

  - Thus the temperature changes are not independent:

$$dT_a = -\frac{T_a}{T_b} dT_b$$

- But

$$dH = dH_a + dH_b = C_P(dT_a + dT_b)$$

  - Substituting for dT_a gives:

$$dH = C_P \left(1 - \frac{T_a}{T_b}\right) dT_b$$

- At equilibrium at constant U and P,

$$T = T_a = T_b$$

- Suppose that the new constraints led to an increase in T_b.
  - Then $T_a/T_b < 1$, $dT_b > 0$ and $dH_{S,P} > 0$ and the system was already stable.
- Suppose that the new constraints led to an increase in T_a.
  - Then $T_a/T_b > 1$, $dT_a > 0$, $dT_b < 0$ and $dH_{S,P} > 0$ and the system was already stable.
- When a system in stable equilibrium requires work to move to another state, the reverse process is spontaneous and can do work on the surroundings.

Free Energy

- Can be defined as the maximum amount of work that can be associated with a constant T process.

- Consider the condition for equilibrium or spontaneity:

$$T_{surr}dS \geq dU - dw$$

where the equal sign applies to equilibrium and $T_{surr} = T$.

- Consider work having two components:

$$dw = -P_{ext}dV + dw'$$

  - $-P_{ext}dV$ represents the work done in moving the boundaries of the system.
  - dw' is all other forms of work.
- Thus the condition for spontaneity may be written:

$$T_{surr}dS - dU \geq P_{ext}dV - dw'$$

where

  - the left hand side depends only on state variables
  - The equality holds for reversible processes
  - The inequality holds for irreversible processes
  - the right hand side is work done by the system.
- The reversible isothermal process will maximize the work done by the system.
  - This is known as the **Free Energy**

Constraints on Free Energy

- All cases considered are reversible processes.
- Consider the case of constant S and constant V:

$$-\Delta U_{S,V} = -w'_{S,V}$$

  - $-w'_{S,V}$ is the maximum work done by the system, **only** under the constraints of constant S and constant V
- Consider the case of constant T and constant V:

$$T\Delta S_{V,T} - \Delta U_{V,T} = -w'_{V,T}$$

  - Recall that the definition of Helmholtz Free Energy, A

$$A = U - TS$$

  - Therefore

$$-\Delta A_{V,T} = -w'_{V,T}$$

- Similarly it may be shown:
  - At constant S and P:

$$-\Delta H_{S,P} = -w'_{S,P}$$

  - At constant T and P:

$$-\Delta G_{T,P} = -w'_{T,P}$$

- Consider further A the Helmholtz free energy:

$$A = U - TS$$

$$dA = dU - TdS$$

  But

$$dU = TdS - PdV$$

  and if PdV is along a reversible path, then

$$dw = -PdV$$

  and

$$dA = dw$$

$$\Delta A = -\int_{V_i}^{V_f} P(V)dV = w$$

- This means that the Helmholtz Free Energy incorporates both internal energy and entropy effects.

A Closer Look at Work

- How can there be any work under the constraint of constant V?
- Consider a variant of the Joule apparatus.
  - The total system is divided into two subvolumes V_I and V_{II} by a frictionless sliding partition.
  - The total volume is fixed.

$$V = V_I + V_{II}$$

  - The system is adiabatically isolated.
- The partition is withdrawn *reversibly.*
  - A reversible adiabatic process is isentropic.
- The system will perform work w'.
  - Since the partition is moved internally, there is no PV work transferred to or from the surroundings.
  - But w' can be calculated from $\int PdV$
- Since the process was carried out at constant S and V,

$$\Delta U_{S,V} = w'_{S,V}$$

- If the system is put in contact with a thermal reservoir, then the constraints become T and V.
  - If the internal partition is moved reversibly, then

$$\Delta A_{T,V} = w'_{T,V}$$

- Consider now the constraints of constant S and P.

  - Two thermal reservoirs at different temperatures T_a and T_b drive a Carnot engine.
  - Run the engine until the temperatures are equal.
  - Work w' will be produced. Therefore:

$$T_f \neq \left(\frac{T_a + T_b}{2} \right)$$

  - Under the constraints of constant S and P, $\Delta H_{S,P} = w'_{S,P}$
- Need to find T_f
  - From the constraint of constant S:

$$0 = dS = dS_a + dS_b = \frac{C_P}{T_a} dT_a + \frac{C_P}{T_b} dT_b$$

$$\frac{dT_a}{T_a} = -\frac{dT_b}{T_b}$$

$$\ln \left(\frac{T_f}{T_a} \right) = -\ln \left(\frac{T_f}{T_b} \right)$$

and

$$T_f = (T_a T_b)^{1/2}$$

  - It can be shown that $T_f < (T_a + T_b)/2$

- The total ΔH is:

$$\Delta H = \Delta H_a + \Delta H_b = C_P(T_f - T_a) + C_P(T_f - T_b)$$

$$\begin{aligned} \Delta H_{S,P} &= C_P((T_a T_b)^{1/2} - T_a) + C_P((T_a T_b)^{1/2} - T_b) \\ &= C_P(2(T_a T_b)^{1/2} - T_a - T_b) \end{aligned}$$

  - Because $T_f < (T_a + T_b)/2$, ΔH is negative and the work is done on the surroundings.

- Consider now the constraints of constant T and P
- An example is a chemical battery which produces work at constant T and P.
  - The reactants in a battery are kept separate until the electrical circuit is complete.
  - When the circuit is complete, electrical work is done on the surroundings.
  - The energy released is the Gibb's Free energy.
  - Energy is released until the free energy is minimized and the battery goes dead.

Multicomponent System and Chemical Potential

- Consider two systems at the same T and P and allow them to interact by exchanging molecules.
- Some examples:
  - Liquid water in contact with water vapour. The boundary between the two phases is the open surface of the liquid.
  - A container of hydrogen in contact with a container of deuterium. The two isotopes will spontaneously mix.

  - Cu(s) in contact with Ag(s). The two metals will spontaneously mix.
  - Oil floating on water. Very little mixing will occur.
- Consider the equilibration of hydrogen and deuterium at constant T and P.
  - The appropriate thermodynamic potential is G, which is extensive.

$$G(total) = G_I + G_{II}$$

where G_I and G_{II} are the Gibbs Free Energy at *any* time in the process.

  - What is going to change is the number of moles of each species in each subsytem.
  - Therefore G_I and G_{II} depend on n_1 and n_2, the number of moles of each species in each subsystem:

$$G_I = G_I(n_1, n_2); G_{II} = G_{II}(n_1, n_2)$$

  - Spontaneous mixing occurs and thus $G(total)$ is expected to decrease:

$$dG_I = \left(\frac{\partial G_I}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G_I}{\partial n_2}\right)_{T,P,n_1} dn_2$$

$$dG_{II} = \left(\frac{\partial G_{II}}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G_{II}}{\partial n_2}\right)_{T,P,n_1} dn_2$$

  - Conservation of mass means:

$$dn_1(\text{container 1}) = -dn_1(\text{container 2})$$

$$dn_2(\text{container 1}) = -dn_2(\text{container 2})$$

  - Therefore:

$$dG(total) = dG_I + dG_{II} =$$

$$\left[\left(\frac{\partial G_I}{\partial n_1}\right)_{T,P,n_2} - \left(\frac{\partial G_{II}}{\partial n_1}\right)_{T,P,n_2}\right] dn_1$$

$$+ \left[\left(\frac{\partial G_I}{\partial n_2}\right)_{T,P,n_1} - \left(\frac{\partial G_{II}}{\partial n_2}\right)_{T,P,n_1}\right] dn_2$$

where dn_1 and dn_2 are with reference to container I.

- The process occurs until $dG = 0$.
  - This may occur in two ways. Either:

$$dn_1 = dn_2 = 0$$

or:

$$\left(\frac{\partial G_I}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial G_{II}}{\partial n_1}\right)_{T,P,n_2}$$

and

$$\left(\frac{\partial G_I}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial G_{II}}{\partial n_2}\right)_{T,P,n_1}$$

  - Note that these partial derivatives have units of molar energies.

- For a one component system:

$$G(T, P, n) = n\overline{G}(T, P)$$

where

$$\overline{G}(T,P) = \frac{G(T,P,n)}{n} = \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

- For a system with more than one component:

$$\overline{G}_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}$$

$$\overline{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1}$$

- These partial molar quantities are also known as chemical potentials:

$$\mu_i = \overline{G}_i$$

- Consider again, the mixing of H_2 and D_2:
- The process will continue until the chemical potential of one component equals the chemical potential of that component throughout the system.

- For a one-component one-phase system at equilibrium, T and P are required to be uniform throughout the system.
- Uniform chemical potential for each component in all phases is an additional requirement for equilibrium in a many component or many phase system.
- In the case of liquid water and vapour
  - There are two phases
  - At equilibrium the chemical potential of the vapour is equal to that of the water.
- In the case of oil floating on water:
  - Traces of oil dissolve into the water and water dissolves into the oil until the chemical potential of the oil in the oil phase is equivalent to the chemical potential of the oil dissolved in the water.
  - The chemical potential of the water dissolved in oil and the chemical potential of the water are equal.

More about Chemical Potential

- Recall the master equation:

$$dU = TdS - PdV$$

and the following definitions of the other thermodynamic potentials:

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS$$

which upon substitution in the master equation, yield the following differentials:

$$dH = TdS + VdP$$

$$dA = -PdV - SdT$$

$$dG = VdP - SdT$$

- It can be shown

$$\mu_i = \left(\frac{\partial U_i}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H_i}{\partial n_i}\right)_{S,P,n_j}$$

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

$$= -T\left(\frac{\partial S_i}{\partial n_i}\right)_{U,V,n_j}$$

Uniformity of Chemical Potential

- Consider a system with
    - c components
    - ϕ phases
    - All phases in contact with each other (directly or indirectly).
    - Assume system is closed.
- The master equation for a particular phase α is:

$$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_{i=1}^{c} \mu_i^\alpha dn_i^\alpha$$

- Consider now the total internal energy of the system:

$$dU = dU^\alpha + dU^\beta + \ldots + dU^\phi$$

$$= T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_{i=1}^{c} \mu_i^\alpha dn_i^\alpha$$

$$+T^\beta dS^\beta - P^\beta dV^\beta + \sum_{i=1}^{c} \mu_i^\beta dn_i^\beta$$

$$+\ldots$$

$$+T^\phi dS^\phi - P^\phi dV^\phi + \sum_{i=1}^{c} \mu_i^\phi dn_i^\phi$$

- The natural variables of U are (S, V, n_i).
- If all these variables are maintained constant:

$$dS = dS^\alpha + dS^\beta + \ldots + dS^\phi = 0$$

$$dV = dV^\alpha + dV^\beta + \ldots + dV^\phi = 0$$

$$dn_i = dn_i^\alpha + dn_i^\beta + \ldots dn_i^\phi = 0,$$

$$i = 1, 2, \ldots, c$$

- If the system has reached equilibrium, then U is minimized and

$$dU_{S,V,n_1,n_2,\ldots,n_c} = 0$$

- This system has $c+2$ variables for each phase ϕ for a total of $\phi(c+2)$ variables.
- Equilibrium of the *entire* system imposes $c+2$ constraints
  - This reduces the number of independent variables to $(\phi-1)(c+2)$.
  - For example, this could be used to eliminate all the variables pertaining to phase α. Thus:

$$\begin{gathered} dU_{S,V,n_1,n_2,\ldots,n_c} = 0 \\ = (T^\beta - T^\alpha)dS^\beta - (P^\beta - P^\alpha)dV^\beta \\ +(\mu_1^\beta - \mu_1^\alpha)dn_1^\beta + \ldots + (\mu_c^\beta - \mu_c^\alpha)dn_c^\beta + \ldots \\ +(T^\phi - T^\alpha)dS^\phi - (P^\phi - P^\alpha)dV^\phi \\ +(\mu_1^\phi - \mu_1^\alpha)dn_1^\phi + \ldots + (\mu_c^\phi - \mu_c^\alpha)dn_c^\phi \end{gathered}$$

  - Each of the variables in this equation are independent.
  - Therefore each of the coefficients of each of these variables must be zero. i.e.

$$\begin{gathered} T^\beta - T^\alpha = 0 \\ P^\beta - P^\alpha = 0 \\ \mu_1^\beta - \mu_1^\alpha = 0 \\ \text{etc.} \\ \mu_c^\phi - \mu_c^\alpha = 0 \end{gathered}$$

- Thus, throughout the system:
  - Temperature is uniform

$$T^\alpha = T^\beta = \ldots = T^\phi = T$$

  - Pressure is uniform

$$P^\alpha = P^\beta = \ldots = P^\phi = P$$

  - Chemical potential of each component is uniform.

$$\begin{gathered} \mu_1^\alpha = \mu_1^\beta = \ldots = \mu_1^\phi \\ \text{etc.} \\ \mu_c^\alpha = \mu_c^\beta = \ldots = \mu_c^\phi \end{gathered}$$

This is the condition for multiphase, multicomponent equilibrium

The Phase Rule

(see Section 6.6)

- Consider the criterion for equilbrium of some component, i, among the ϕ phases:

$$\mu_i^\alpha = \mu_i^\beta = \ldots = \mu_i^\phi$$

  - This establishes a set of relationships (in addition to those established from the master equation) among n_i^ϕ, such that these are not independent of each other.
  - These relationships provide $(\phi - 1)$ constraints on component i for a total of $c(\phi - 1)$ constraints.
- In addition, the fact that T and P are constant removes $2\phi - 2$ degrees of freedom.
  - But T and P are just a specific instance of external intensive variables.
  - There are systems in which other external intensive variables could be important (such as surface energy, external magnetic or electrical fields, external force, etc.)
  - Therefore use I to describe the number of external intensive variables and generally the condition of uniformity of the external intensive variables removes $I\phi - I$ degrees of freedom.

How many degrees of freedom are left?

- For c components, there are $c - 1$ independent mole fractions
- Each of ϕ phases is described by $c - 1 + I$ intensive variables for a total of $\phi(c - 1 + I)$ variables
- Because at equilibrium the *external* intensive variables are uniform throughout the system, this is reduced by $\phi I - I$.
  - This leaves $\phi(c - 1) + I$
- The uniformity of chemical potential throughout the system gives $\phi - 1$ constraints for each of c components.
  - Therefore the number of independent variables is:

$$\phi(c - 1) + I - c(\phi - 1)$$

$$c - \phi + I$$

- Thus the phase rule is:

"The number of truly independent intensive variables in a system composed of c independent components among ϕ phases subject to I external intensive variables is $c - \phi + I$"

Calculation of Chemical Potentials

- Consider the master equation for a one component system

$$dU = TdS - PdV$$

- Add $d(PV - TS)$ to both sides:

$$dU + d(PV - TS) = TdS - PdV + d(PV - TS)$$

$$= TdS - PdV + PdV + VdP - TdS - SdT$$

$$= VdP - SdT$$

- The Legendre transform of U with P and T as the natural variables is G

$$dG = dU + d(PV - TS) = VdP - SdT$$

- But:

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

- Therefore

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

  and

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

- Since S and V are always positive then (for a one component system)
  - G always increases with P at constant T
  - G always decreases with T at constant P
- For each component of a multicomponent system:

$$d\mu_i = \overline{V}_i dP - \overline{S}_i dT$$

  where
  - $\overline{V}_i$ is the partial molar volume
  - $\overline{S}_i$ is partial molar entropy.
- What is the physical significance of partial molar volume?

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

- Experimentally this can be determined through

$$\overline{V}_i = \frac{V(\text{after addition}) - V(\text{before addition})}{\#\text{ moles added}}$$

  where the number of moles added is the smallest amount possible that yields an observable change.
- In a multicomponent system, the volume change may be either positive or negative.
  - This reflects that nature of molecular interactions among the various components in the system.
  - If the interaction of the added molecules with the molecules already in the mixture is strongly attractive, then the volume will tend to decrease.
  - If the interaction of the added molecules with the molecules already in the mixture is strongly repulsive, then the volume will tend to increase.

More about Chemical Potential and Free Energy

- For a system of c components:

$$G(total) = \mu_1 n_1 + \mu_2 n_2 + \ldots + \mu_c n_c = \sum_{i=1}^{c} \mu_i n_i$$

- In differential form

$$dG(total) = \sum_{i=1}^{c}(\mu_i dn_i + n_i d\mu_i) =$$

$$\sum_{i=1}^{c} \mu_i dn_i + \sum_{i=1}^{c} n_i d\mu_i$$

- Substituting for $d\mu_i$ gives:

$$dG = \sum_{i=1}^{c} \left[\mu_i dn_i + n_i(\overline{V}_i dP - \overline{S}_i dT)\right]$$

- Collecting terms:

$$dG = \sum_{i=1}^{c} \mu_i dn_i + \left[\sum_{i=1}^{c} n_i \overline{V}_i\right] dP - \left[\sum_{i=1}^{c} n_i \overline{S}_i\right] dT$$

- But:

$$\left[\sum_{i=1}^{c} n_i \overline{V}_i\right] = V \text{ and } \left[\sum_{i=1}^{c} n_i \overline{S}_i\right] = S$$

- Therefore:

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

  and

$$\sum_{i=1}^{c} n_i d\mu_i = VdP - SdT$$

  or

$$0 = VdP - SdT - \sum_{i=1}^{c} n_i d\mu_i$$

- Thus if P and T are held constant then:

$$\sum_{i=1}^{c} n_i d\mu_i = 0$$

  (This is the Gibbs-Duhem equation)

One component Ideal Gases

- Generally: $\mu_i = \overline{G} = G/n$. Thus:

$$\Delta\mu = \int d\mu = \int_{P_i}^{P_f} \overline{V}(T_i, P)dP - \int_{T_i}^{T_f} \overline{S}(T, P_f)dP$$

if we chose to change the T first then P.

  - For an ideal gas, the first term is:

$$\int_{P_i}^{P_f} \overline{V}(T, P)dP = \int_{P_i}^{P_f} \frac{RT_i}{P} dP = RT_i \ln\left(\frac{P_f}{P_i}\right)$$

  - For the second term, first the definition of entropy must be considered;

$$dS = \frac{dq_P}{T} = \frac{dH_P}{T} = \frac{5}{2}\frac{nR}{T}dT$$

$$
\begin{aligned}
\frac{\overline{S}(T,P)}{R} &= \frac{5}{2}\ln(T) + \text{constant} \\
&= \ln\left[\frac{T^{5/2}}{P}(\text{constant})\right]
\end{aligned}
$$

  - Recall that entropy is on an absolute scale, therefore the constant matters.

- Sackur (1911) showed that the constant depends on the molecular mass:

$$
\begin{aligned}
\frac{\overline{S}(T,P)}{R} &= \ln\left[\frac{T^{5/2}M^{3/2}}{P}(\text{another constant})\right] \\
&= \ln\left[\frac{T^{5/2}M^{3/2}}{P}(0.311968\ \text{g}^{-3/2}\text{K}^{-5/2}\text{atm})\right]
\end{aligned}
$$

  - This is the Sackur-Tetrode equation.
  - Tetrode (1912) showed that the constant was truly universal.

- Carrying out the integration:

$$
-\int_{T_i}^{T_f} \overline{S}(T,P_f)dP = -\frac{5}{2}R(T_i - T_f)
$$

$$
-R\left[T_f \ln\left(\frac{CM^{3/2}T_f^{5/2}}{P_f}\right) - T_i \ln\left(\frac{CM^{3/2}T_i^{5/2}}{P_f}\right)\right]
$$

where C is the Sackur-Tetrode constant.

- Therefore:

$$
\begin{aligned}
\Delta\mu = RT_i \ln\left(\frac{CM^{3/2}T_i^{5/2}}{P_i}\right) \\
-RT_f \ln\left(\frac{CM^{3/2}T_f^{5/2}}{P_f}\right) + \frac{5}{2}R(T_f - T_i)
\end{aligned}
$$

The Standard State

- Chemical potentials are not on an absolute scale, but are with respect to an arbitrarily chosen reference state.
- If the reference state is the ideal gas at a pressure of 1 bar, then

$$
\mu(T,P) = \mu^\circ(T) + RT\ \ln\left(\frac{P}{1\ \text{bar}}\right)
$$

  - This definition of the standard state requires that P be expressed in the units of the reference state, bars.

Fugacity and the One-Component Real Gas

- The ideal gas law $P\overline{V} = RT$ allows the easy integration of:

$$
\int_{1\ \text{bar}}^{P} \overline{V}(T,P)dP
$$

  - but equations of state that describe real gases often do not have such a convenient functional form.
  - Numerical integration of tabulated data is inconvenient.
- G. N. Lewis (1901) proposed that f, fugacity be defined as:

$$d\mu = \frac{RT}{f} df = RT\ d\ \ln f; \qquad \text{constant } T$$

  - Fugacity has the units of pressure
  - At low P, $f \rightarrow P$. Therefore, integrating from some low pressure P_0 (such that the ideal gas equation of state is valid) to a higher pressure P gives:

$$\mu(P,T) - \mu(P_0,T) = RT\ \ln f\ -\ RT\ \ln P_0$$

    where f is the fugacity of the gas at pressure P.

- Since the standard state is defined with respect to 1 bar pressure:

$$\mu(P_0,T) - \mu^\circ(1\text{ bar},T) = RT\ \ln P_0$$

- Therefore

$$\mu(P,T) - \mu^\circ(1\text{ bar},T) = RT\ \ln f$$

  and **all** the nonideal behaviour is described by f. The standard state may be thought of as the real gas behaving ideally at 1 bar pressure.
- Uniform chemical potential means uniform fugacity.
  - Fugacity may be considered a property of all phases, not just gases.

Calculation of Fugacity

- For a pure compound at constant T:

$$d\mu_T = \left(\frac{\partial \mu}{\partial P}\right)_T dP = \overline{V} dP = \frac{RT}{f} df$$

- Subtracting $(RT/P)dP = RT\ d\ \ln P$ from both sides gives:

$$\left(\overline{V} - \frac{RT}{P}\right) dP = RT(d\ \ln f - d\ln P)$$

- Integrating from $P = 0$ to the P of interest gives:

$$RT \ln\left(\frac{f}{P}\right) = \int_0^P \left(\overline{V} - \frac{RT}{P}\right) dP$$

- $\overline{V}$ may be described through the compressibility factor Z:

$$Z \equiv \frac{PV}{RT}$$

$$Z(P) = 1 + A_1(T)P + A_2(T)P^2 + \ldots$$

$$Z(V) = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2}$$

- Thus the integral becomes:

$$\ln\left(\frac{f}{P}\right) = \int_0^P \frac{Z(P)-1}{P} dP$$

- At P sufficiently low for the virial expansion to the second coefficient to be accurate this integral becomes:

$$\begin{aligned}
\int_0^P \frac{Z(P)-1}{P} dP &\cong \int_0^P \frac{B(T)}{P\overline{V}} dP \\
&= \frac{B(T)}{RT} \int_0^P \frac{RT}{P\overline{V}}\, dP \\
&= \frac{B(T)}{RT} \int_0^P \frac{1}{Z}\, dP \\
&\cong \frac{B(T)}{RT} \int_0^P \frac{1}{1 + B(T)/\overline{V}}\, dP \\
&\cong \frac{B(T)}{RT} \int_0^P dP = \frac{B(T)P}{RT} \\
\ln\left(\frac{f}{P}\right) &= \frac{B(T)P}{RT}
\end{aligned}$$

Therefore

$$f \cong P \exp\left[\frac{B(T)P}{RT}\right]$$

Recalling that $\exp x \cong\ 1 + x$ for small x:

$$f \cong P\left(1 + \frac{B(T)P}{RT}\right) \cong P\left(1 + \frac{B(T)}{\overline{V}}\right) = PZ$$

- Recalling that T_B, the Boyle temperature, is the temperature at which $B(T) = 0$, it can be shown:
  - $f < P$ when $T < T_B$
  - $f > P$ when $T > T_B$

Fugacity and Other Equations of State

- Consider the van der Waals equation of state:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

- In terms of dimensionless variables this is:

$$\tilde{P} = \frac{\tilde{T}}{(\tilde{V} - 1)} - \frac{1}{\tilde{V}^2}$$

  - Where

$$\tilde{V} = \frac{\overline{V}}{b}$$

$$\tilde{P} = \frac{Pb^2}{a}$$

$$\tilde{T} = \frac{T}{T_B}$$

- It can be shown that

$$\ln\left(\frac{f}{P}\right) = \ln\left[\frac{\tilde{T}}{\tilde{P}(\tilde{V}-1)}\right] + \frac{1}{(\tilde{V}-1)} - \frac{2}{\tilde{T}\tilde{V}}$$

- The quantity f/P is defined as the fugacity coefficient:

$$\Phi = \frac{f}{P}$$