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Lecture Notes - General Thermodynamics

Prof. Yarger's Hand Written Lecture Notes

ASU BCH 341 - 'Physical Chemistry With A Biological Focus' - i.e. BioPhysical Chemistry
BioPchem: Thermo

Lecture Notes - Set 3 - Topics:

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Summary

For simple closed systems, the general Extremum principle can be written as:

General Extremum Principle

$$dS - \frac{1}{T^*}\,dU - \frac{P^*}{T^*}\,dV \geq 0$$

or

$$dU - T^*\,dS + P^*\,dV \leq 0$$

Entropy Maximum Principle: (fixed $U, V, \underline{N}$)

For a system with fixed $U, V, \underline{N}$,

$$\Rightarrow \Delta S \geq 0$$ for any spontaneous process

Thus, the final Equilibrium state for any isolated system (i.e, $U, V, \underline{N}$ fixed) is that state which maximizes the Entropy of the System.

Energy Minimum Principle: (fixed $S, V, \underline{N}$)

From the general Extremum principle we see that,

$$\Rightarrow \Delta U \leq 0$$ for any spontaneous process

The final Equilibrium state for any system where $S, V, \& \underline{N}$ are fixed is that state which minimizes the Energy of the System.

In summary, we have found that the 2nd law provides an Extremum principle which can be used to determine the final Equilibrium state of a system when any of its internal Constraints are removed. All of these Extremum principles simply boil down to the fact that a system will ultimately seek a final state which maximizes the Total Entropy of the system + surroundings. The various Thermodynamic potentials recast this statement in terms of System variables, i.e., the Entropy change of the Surroundings under certain conditions (i.e., P^* or T^* fixed) can be Expressed as changes in system variables.

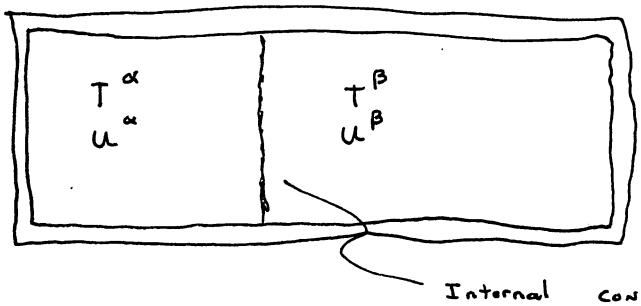
Variables Constrained	Thermodynamic Extremum
$U, V, \underline{N}$	S maximized
$S, V, \underline{N}$	U minimized
$T^*, V, \underline{N}$	A minimized
$T^*, P^*, \underline{N}$	G "
$S, P^*, \underline{N}$	H "

It is important to note that these Extremum principles are fundamental. That is, they are valid for any general system regardless of the number of chemical components or phases present within the system. Our only restriction at this point is that the System be simple ($P^* dV$ work only) and closed ($\underline{N}$ fixed). The Extremum principle can easily be extended to situations where other types of work are allowed and also open systems.

We will see how the Extremum principle can be used to determine the final Equilibrium state of the system, i.e., how the Energy, mass & volume is distributed both within the system and between the system and surroundings.

I. Thermal Equilibrium

Consider the isolated composite system:



Extremum: $\Delta S \geq 0$

$$dS = dS^\alpha + dS^\beta$$ S is Extensive

$$dS = \frac{1}{T^\alpha} du^\alpha + \frac{1}{T^\beta} du^\beta$$ assume $dV^\alpha, dV^\beta = 0$

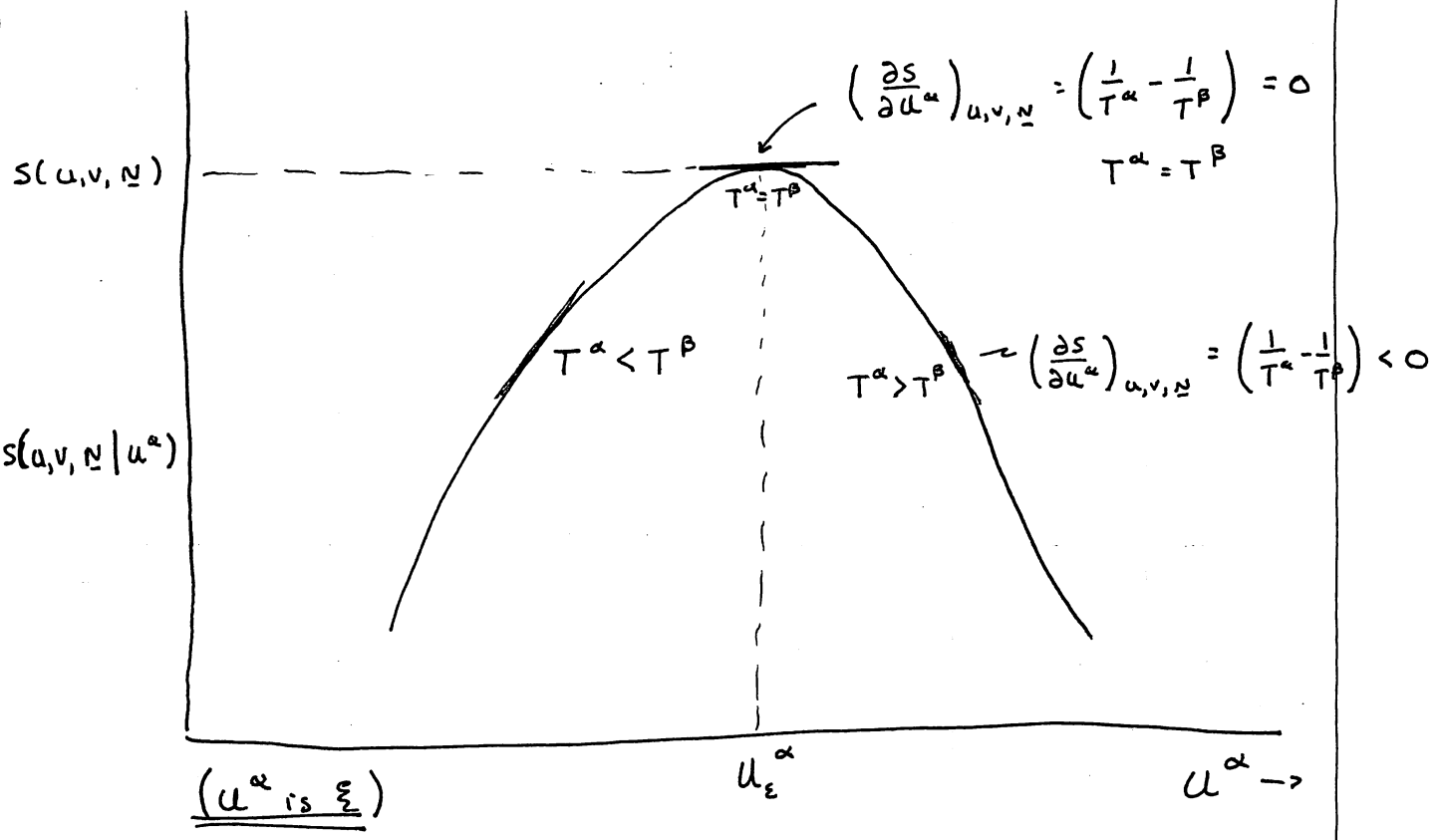
by the closure condition: $du^\beta = -du^\alpha$

$$dS = \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right) du^\alpha \geq 0$$

du^α → "Thermodynamic responce" $d\xi$

$\left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right)$ → "Thermodynamic driving force": → gradient in temperature

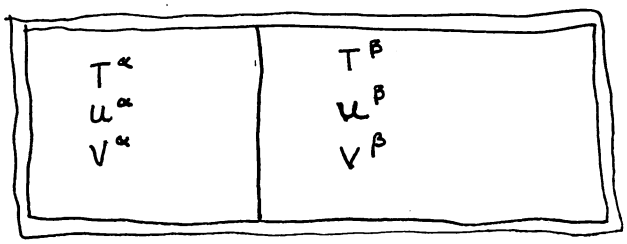
- if $T^\alpha > T^\beta \Rightarrow du^\alpha < 0$, heat flows from left to right with internal entropy production.
- if $T^\alpha < T^\beta \Rightarrow du^\alpha > 0$, heat flows from right to left with internal entropy production.
- if $T^\alpha = T^\beta \Rightarrow du^\alpha = 0$, no heat flow, no internal Entropy production → This is the final Equilibrium State!



S is a maximum when $T^\alpha = T^\beta$. This would be the final Equilibrium if the internal constraint were removed.

Mechanical Equilibrium

Again consider the isolated composite system:



$\Delta S \geq 0$

$$dS = dS^\alpha + dS^\beta$$

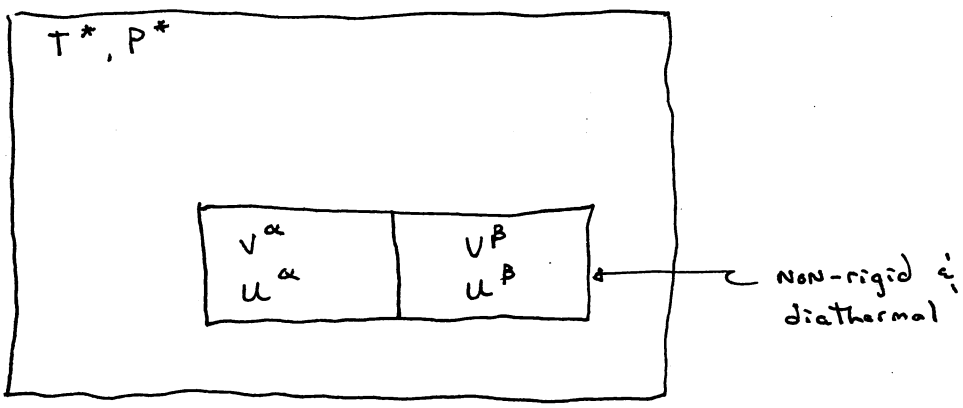
$$= \frac{1}{T^\alpha} du^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha + \frac{1}{T^\beta} du^\beta + \frac{P^\beta}{T^\beta} dV^\beta$$

closure condition: $du^\beta = -du^\alpha$ $\qquad$ $dV^\beta = -dV^\alpha$

$$dS = \underbrace{\left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right)}_{\text{Thermodynamic driving force}} \underbrace{du^\alpha}_{d\xi^\alpha} + \underbrace{\left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta}\right)}_{\text{Thermodynamic driving force}} \underbrace{dV^\alpha}_{d\xi^\beta}$$

@ Equilibrium, $T^\alpha = T^\beta$ & $P^\alpha = P^\beta$

Now Consider the same composite system we just looked at, but in an isothermal isobaric surroundings at T^* & P^*:



General Extremum Principle:

$$dS = \frac{1}{T^*}dU - \frac{P^*}{T^*}dV \geq 0$$

Now consider changes in the internal Energy & volume distribution within the system. Here, however, because the system is non-rigid & diathermal, <u>both</u> U^α & U^β <u>and</u> V^α & V^β are independent variables.

Expand:

$$dS = dS^\alpha + dS^\beta$$

$$= \frac{1}{T^\alpha}dU^\alpha + \frac{P^\alpha}{T^\alpha}dV^\alpha + \frac{1}{T^\beta}dU^\beta + \frac{P^\beta}{T^\beta}dV^\beta$$

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

$$dV = dV^\alpha + dV^\beta$$

$$0 \leq \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right)dU^\alpha + \left(\frac{1}{T^\beta} - \frac{1}{T^\alpha}\right)dU^\beta + \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta}\right)dV^\alpha + \left(\frac{P^\beta}{T^\beta} - \frac{P^\alpha}{T^\alpha}\right)dV^\beta$$

@ Equilibrium: $T^\alpha = T^*$; $T^\beta = T^*$; $P^\alpha = P^*$; $P^\beta = P^*$

For a more interesting application consider Equilibrium between a liquid droplet and its vapor. For now, we will consider the simple problem of only thermal & mechanical Equilibrium. We will not yet consider mass exchange between the liquid and its vapor.

P^*, T^* ← we will consider the vapor to be the surroundings.

General Extremum Principle:

$$dU - T^* dS + P^* dV \leq 0$$

We will consider our system to be the liquid droplet + surface.

$$dU = dU^\beta + dU^\gamma$$
$$dS = dS^\beta + dS^\gamma$$
$$dV = dV^\beta$$

all of these variables are not independent since they are related by their own fundamental Eqns.

We will choose to expand dU^β & dU^γ (it wouldn't have made any difference if we expanded dS^β & dS^γ instead)

$$dU^\beta = T^\beta dS^\beta - P^\beta dV^\beta$$

$$dU^\gamma = T^\gamma dS^\gamma + \sigma\, dA$$

$$(T^\beta - T^*)\, dS^\beta + (T^\gamma - T^*)\, dS^\gamma - (P^\beta - P^*)\, dV^\beta + \sigma\, dA \leq 0$$

Note that V^β & A are NOT independent:

$$V^\beta = \tfrac{4}{3}\pi r^3 \qquad A = 4\pi r^2$$

$$dV^\beta = 4\pi r^2 \qquad dA = 8\pi r$$

$$\Rightarrow \boxed{dA = \frac{2\, dV^\beta}{r}}$$

$$(T^\beta - T^*)\, dS^\beta + (T^\gamma - T^*)\, dS^\gamma - \left(P^\beta - P^* - \frac{2\sigma}{r}\right) dV^\beta \leq 0$$

At the final Equilibrium state, the expression is at an Extremum so that:

for thermal Equilibrium, $T^\beta = T^*$; $T^\gamma = T^*$

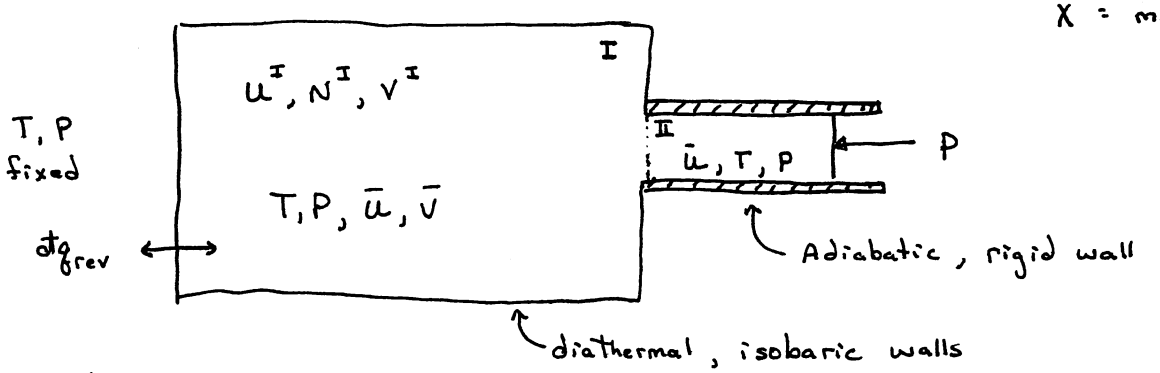
also, for mechanical Equilibrium,

$$\boxed{P^\beta - P^* = \frac{2\sigma}{r}}$$

Extension of Fundamental Equations to Open Systems

For simplicity lets assume an open single-component system. We need to derive appropriate expressions for the 1st & 2nd Laws. To do this, let's consider a <u>composite</u> system where we reversibly inject mass, dN, from the right-hand side to the left-hand side:

$\bar{X}$ = molar quantity



<u>1st law</u>

The composite system is closed & we have:

$$dU^I + dU^{II} = dU^I + \bar{u}\,dN^{II} = dq_{rev} + dw_{rev}$$

by closure: $dN^{II} = -dN^I$

also, $dw_{rev} = -P\,dV^I - P\,dV^{II}$

$$dV^{II} = \bar{V}\,dN^{II} = -\bar{V}\,dN^I$$

$$\Rightarrow \quad dU^I - \bar{u}\,dN^I = dq_{rev} - P\,dV^I + P\bar{V}\,dN^I$$

or

$$\boxed{dU^I = dq_{rev} - P\,dV^I + (\bar{u} + P\bar{v})\,dN^I}$$

Now consider the <u>2nd law</u> applied to the composite system:

For reversible injection:

$$dS^I + dS^{II} = \frac{dq_{rev}}{T}$$

$$dS^{II} = \bar{S}\,dN^{II} = -\bar{S}\,dN^I$$

$$\Rightarrow \quad \boxed{dS^I = \frac{dq_{rev}}{T} + \bar{S}\,dN^I}$$

Now, combining the 1st & 2nd laws:

$$dU^I = TdS^I - PdV^I + (\bar{u} + PV - T\bar{S})\, dN^I$$

or

$$\boxed{\begin{aligned} dU^I &= TdS^I - PdV^I + \bar{G}\, dN^I \\ dS &= \frac{1}{T} dU^I + \frac{P}{T} dV^I - \frac{\bar{G}}{T} dN^I \end{aligned}}$$

Fundamental Eqns for an open single-component system

where $\bar{G}$ is the molar free energy of the pure component at the same T & P as the system.

Note: $\bar{G} = \left(\frac{\partial U}{\partial N}\right)_{S,V}$ valid for a pure system.

These fundamental Equations for open systems can easily be extended to multi-component systems. For an open system composed of C chemical components, the fundamental equations for dU & dS are:

$$\boxed{\begin{aligned} dU &= TdS - PdV + \sum_{i=1}^{C} \mu_i\, dN_i \\ dS &= \frac{1}{T} dU + \frac{P}{T} dV - \sum_{i=1}^{C} \frac{\mu_i}{T} dN_i \end{aligned}}$$

where,

$$\boxed{\mu_i \equiv \left(\frac{\partial U}{\partial N_i}\right)_{S,V,\underline{N}'} = \left(\frac{\partial S}{\partial N_i}\right)_{U,V,\underline{N}'}}$$

μ_i is called the "chemical potential"

$\underline{N}'$, The prime is to remind one to exclude the i^{Th}-component of interest.

These equations are valid for open systems regardless of the number of phases present, provided that the only work is PdV work.

Also, $\mu_i \equiv \bar{G}_i = \bar{U}_i - T\bar{S}_i + P\bar{V}_i$

or

$\mu_i \equiv \bar{G}_i = \bar{H}_i - T\bar{S}_i$

Other Thermodynamic Potentials for Open Systems

The complete set of thermodynamic functions can be obtained through Legendre transforms of dU:

$$H(S,P,\underline{N}) \equiv U + PV \qquad dH = TdS + VdP + \sum_{i=1}^{c} \mu_i dN_i$$

$$A(T,V,\underline{N}) \equiv U - TS \qquad dA = -SdT - PdV + \sum_{i=1}^{c} \mu_i dN_i$$

$$G(T,P,\underline{N}) \equiv U - TS + PV \qquad dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dN_i$$

$$U(S,V,\underline{N}) \equiv U \qquad dU = TdS - PdV + \sum_{i=1}^{c} \mu_i dN_i$$

$$S(U,V,\underline{N}) \equiv S \qquad dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_{i=1}^{c} \frac{\mu_i}{T} dN_i$$

Of course, Legendre transforms of the above equations with respect to $\mu_i N_i$ conjugate pairs can also be obtained. These Equations are sometimes useful (i.e., nucleation theory,) but are less well known. We'll will introduce them when they are needed later in the course.

From the above Equations we see that the chemical potential, μ_i, can be defined in several equivalent ways:

$$\mu_i \equiv \left(\frac{\partial U}{\partial N_i}\right)_{S,V,\underline{N}'} = -T\left(\frac{\partial S}{\partial N_i}\right)_{U,V,\underline{N}'} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,\underline{N}'} = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,\underline{N}'}$$

$$\frac{\mu_i}{T} = -\left(\frac{\partial S}{\partial N_i}\right)_{U,V,\underline{N}'} \quad \text{i} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,\underline{N}'}$$

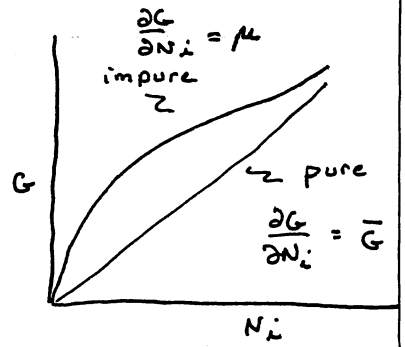
Note that each one of these defining Equations are derivatives of a thermodynamic potential with respect to N_i, keeping the natural variables of the potential fixed.

Recall, for a single component system, we identified the chemical potential with the molar free energy.

$$\mu \equiv \frac{G}{N} \equiv \bar{G}$$ single component system

However, for a multi component system, μ_i, can be identified as the "partial molar" free Energy of component i.

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,\underline{N}'} \equiv \bar{G}_i$$



The fundamental Eqns of multicomponent systems also provides additional Maxwell relations. (The most useful are the following):

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\underline{N}} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,\underline{N}'} \equiv -\bar{S}_i$$ partial molar Entropy

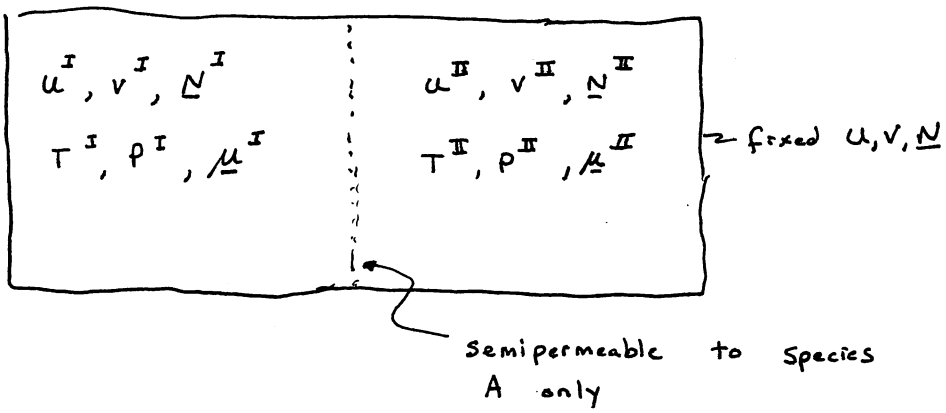
$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\underline{N}} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,\underline{N}'} \equiv \bar{V}_i$$ partial Molar volume

Recall, for a single component system:

$$\left(\frac{\partial \bar{G}}{\partial T}\right)_{P,N} = -\bar{S} \quad \& \quad \left(\frac{\partial \bar{G}}{\partial P}\right)_{T,N} = \bar{V}$$

Chemical Potential as an "Escaping Tendency"

Consider a composite isolated system separated into two parts by a semipermeable membrane.



For the isolated system, the final equilibrium state is that which maximizes the total entropy of the system.

$$dS = dS^I + dS^{II}$$

$$dS^I = \frac{1}{T^I} dU^I - \frac{\mu_A^I}{T^I} dN_A^I \qquad V^I \& N_{i\neq A}^I \text{ fixed}$$

$$dS^{II} = \frac{1}{T^{II}} dU^{II} - \frac{\mu_A^{II}}{T^{II}} dN_A^{II} \qquad V^{II} \& N_{i\neq A}^{II} \text{ fixed}$$

by closure, $dU^I = -dU^{II}$

$dN_A^I = -dN_A^{II}$

$$\Rightarrow dS = \left(\frac{1}{T^I} - \frac{1}{T^{II}}\right) dU^I - \left(\frac{\mu_A^I}{T^I} - \frac{\mu_A^{II}}{T^{II}}\right) dN_A^I$$

at equilibrium, S is a maximum $\Rightarrow dS = 0$

for $dS = 0 \Rightarrow$ $T^I = T^{II}$ Thermal Equilibrium

$\&$ $\mu_A^I = \mu_A^{II}$ Chemical Equilibrium

Chemical Equilibrium for species A is achieved when the chemical potential of A is the same on both sides of the membrane. Thus, Even if the pressure & composition of each side is different, chemical Equilibration occurs when

$$\mu_A^{I}(T, P^{I}, \underline{N}^{I}) = \mu_A^{II}(T, P^{II}, \underline{N}^{II})$$

We can view μ_A as an "escaping tendency" for component (or species) A by noting that away from equilibrium,

$$dS = -\frac{1}{T}(\mu_A^{I} - \mu_A^{II})\, dN_A^{I} \quad \text{if } T \text{ is equilibrated}$$

if $\mu_A^{I} > \mu_A^{II} \Rightarrow N_A^{I}$ will decrease to increase S.

if $\mu_A^{I} < \mu_A^{II} \Rightarrow N_A^{I}$ will increase to increase S.

Thus, the larger the chemical potential of species A, the greater the escaping tendency of A. A will diffuse from region of high chemical potential to a region of low chemical potential. The net flux of A will cease when there is no longer any chemical potential gradient, regardless of whether there exists compositional or pressure gradients.

Chemical Reactions - Prelude

In the previous example we looked at the Equilibration of chemical components between homogeneous phases of a system. We can also apply the general Extremum principle to determine the Equilibrium distribution of mass among various chemical species. And even more generally, these species may also be in different phases.

For Example, consider a closed system whose bulk composition can be described by some mixture of H_2 & Cl_2. Although only 2 independent chemical components are required to specify the bulk composition of the system, the mass can be distributed over a number of chemical species, i.e., $H_2(g)$, $Cl_2(g)$, $HCl(g)$, $HCl(\ell)$, etc.., even $H^+(g)$ & $Cl^-(g)$. At Equilibrium, the mass distribution over the various species is that distribution which satisfies the Extremum principle (i.e. max Entropy of the universe). The Final Equilibrium state of the system is specified if we specify.

$$U, V, N_{H_2}^{ExT}, N_{Cl_2}^{ExT} \qquad 2+c \text{ Total variables}$$

where $N_{H_2}^{ExT}$ & $N_{Cl_2}^{ExT}$ specify the bulk composition of the system - regardless of the species actually present.

We can exploit the Extremum principle to determine the Internal mass distribution over the possible chemical species. For this we need to consider all the possible species

and the possible reactions between them. In our system, over a considerable T & P range we need only consider H_2, Cl_2, and HCl species.

The balance reaction involving these species in the gas phase is given by:

$$H_2\,(g) + Cl_2\,(g) \longleftrightarrow 2\,HCl\,(g)$$

$N_{H_2}^{(g)}$, $N_{Cl_2}^{(g)}$ & $N_{HCl}^{(g)}$ are internal coordinates which define the internal mass distribution. The equilibrium distribution can be determined from the general extremum principle.

For a closed system under isothermal & isobaric conditions, the extremum principle reduces to

$$G(T = T^*, P = P^*) \leq 0$$

at fixed T & P.

$$dG = \mu_{H_2}^{(g)} dN_{H_2}^{(g)} + \mu_{Cl_2}^{(g)} dN_{Cl_2}^{(g)} + \mu_{HCl}^{(g)} dN_{HCl}^{(g)} \leq 0$$

Changes in $N_{H_2}^{(g)}$, $N_{Cl_2}^{(g)}$ & $N_{HCl}^{(g)}$ are <u>NOT</u> independent but are related through the chemical reaction equation:

$$dN_{H_2}^{(g)} = -d\xi$$
$$dN_{Cl_2}^{(g)} = -d\xi$$
$$dN_{HCl}^{(g)} = 2\,d\xi$$

$$\Rightarrow \quad dG = \left(2\mu_{HCl}^{(g)} - \mu_{H_2}^{(g)} - \mu_{Cl_2}^{(g)}\right) d\xi \leq 0$$

at equilibrium, $\quad 2\mu_{HCl}^{(g)} - \mu_{H_2}^{(g)} - \mu_{Cl_2}^{(g)} = 0$

To go further we need to know how to write the chemical potentials of the various species in terms of the T, P & composition of the system.

General Foralism for Multicomponent Homogeneous Systems

We will develop the general thermodynamic formalism for multicomponent single-phase systems (i.e. homogeneous systems.). Ultimately, this will provide the basis of determining the mass distribution within a system at Equilibrium.

I. Euler's Equation (for homogeneous phases)

Recall The fundamental Equation for a general multicomponent system,

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i \, dN_i$$

AlThough this Equation can generally be applied to multiphase assemblages at Equilibrium, we can also apply this Equation to Sinqle homogeneous phases – even if they are metastable.

For a homogeneous phase we can always write:

$S = \Delta V$	where	$\Delta \equiv S/V$	Entropy density
$N_i = n_i V$		$n_i \equiv N_i/V$	number density
$U = uV$		$u \equiv U/V$	Energy density

$$\Rightarrow dU = Td(\Delta V) - PdV + \sum_{i=1}^{C} \mu_i \, d(n_i V)$$

Now suppose we integrate dU over the size of a homogeneous system, i.e., starting from zero we gradually increase the size of our System until it empompasses the Entire phase. Through the integration we are not changing any of the intensive variables of the system, u, s, n_i are all fixed.

So,

$$\Rightarrow \int_0^u du = \left(TS - P + \sum \mu_i n_i\right) \int_0^V dV$$

or

$$u = TSV - PV + \sum_{i=1}^{c} \mu_i n_i V$$

Euler's EqN $\Rightarrow$ for a homogeneous phase.

$$\boxed{u = TS - PV + \sum_{i=1}^{c} \mu_i N_i}$$

This expression is called Euler's Equation which is valid for any homogeneous (single-phase) system where the intensive variables are constant over the entire system (no gradients in the intensive variables are allowed).

It follows directly, that for any homogeneous phase:

$$u = TS - PV + \sum_{i=1}^{c} \mu_i N_i \qquad u(S, V, \underline{N})$$

$$H \equiv u + PV = TS + \sum_{i=1}^{c} \mu_i N_i \qquad H(S, P, \underline{N})$$

$$A \equiv u - TS = -PV + \sum_{i=1}^{c} \mu_i N_i \qquad A(T, V, \underline{N})$$

$$G \equiv u - TS - PV = \sum_{i=1}^{c} \mu_i N_i \qquad G(T, P, \underline{N})$$

$$S = \frac{1}{T}u + \frac{P}{T}V - \sum_{i=1}^{c} \frac{\mu_i}{T} N_i \qquad S(u, V, \underline{N})$$

$$\Phi \equiv u - TS - \sum \mu_i N_i = -PV$$

$$d\Phi = -S\,dT - P\,dV - \sum N_i\, d\mu_i$$

II. Partial Molar Quantities

We can generalize the previous arguments to <u>any Extensive state function</u> of a <u>homogeneous system</u>. Particularly useful are the Euler Relations related to <u>partial molar quantities</u>.

Suppose Y is some extensive state variable. If we expand $Y(T, P, N_1, N_2 \cdots N_c)$:

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{P,\underline{N}} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,\underline{N}} dP + \sum_{i=1}^{c} \left(\frac{\partial Y}{\partial N_i}\right)_{T,P,\underline{N}'} dN_i$$

For a homogeneous system we can integrate dY over the size of the system keeping all of the intensive variables fixed:

we obtain,

$$Y = \sum_{i=1}^{c} \left(\frac{\partial Y}{\partial N_i}\right)_{T,P,\underline{N}'} N_i$$

$$\boxed{Y = \sum_{i=1}^{c} y_i N_i}$$

where $y_i \equiv \left(\frac{\partial Y}{\partial N_i}\right)_{T,P,\underline{N}'}$ "partial molar"

or, dividing the equation by $N \equiv \sum_{i=1}^{c} N_i$

$$\boxed{\begin{array}{l} y = \sum_{i=1}^{c} y_i X_i \quad \leftarrow \text{all variables here are intensive} \\ \text{where,} \\ y \equiv Y/N \qquad \text{molar } y \\ X_i \equiv N_i/N \qquad \text{mole fraction} \\ y_i \equiv \left(\frac{\partial Y}{\partial N_i}\right)_{T,P,\underline{N}'} \qquad \text{partial Molar } Y \end{array}}$$

Examples (valid only for homogeneous single-phase systems)

$$H = \sum_{i=1}^{c} \mathcal{H}_i N_i$$

$$\mathcal{H} = \sum_{i=1}^{c} \mathcal{H}_i X_i \qquad \text{where} \quad \mathcal{H}_i \equiv \left(\frac{\partial H}{\partial N_i} \right)_{T,P,\underline{N}'}$$

$$S = \sum_{i=1}^{c} \mathcal{S}_i N_i$$

$$\mathcal{S} = \sum_{i=1}^{c} \mathcal{S}_i X_i \qquad \text{where} \quad \mathcal{S}_i \equiv \left(\frac{\partial S}{\partial N_i} \right)_{T,P,\underline{N}'}$$

$$V = \sum_{i=1}^{c} \mathcal{V}_i N_i$$

$$\mathcal{V} = \sum_{i=1}^{c} \mathcal{V}_i X_i \qquad \text{where} \quad \mathcal{V}_i \equiv \left(\frac{\partial V}{\partial N_i} \right)_{T,P,\underline{N}'}$$

$$G = \sum_{i=1}^{c} g_i N_i = \sum_{i=1}^{c} \mu_i N_i$$

$$g = \sum_{i=1}^{c} g_i X_i = \sum_{i=1}^{c} \mu_i X_i \qquad \text{where} \quad g_i = \mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T,P,\underline{N}'}$$

etc ...

Graphical Determination of Partial Molar Quantities:

Example: $v = \sum_{i=1}^{c} x_i v_i$

Note: all of the x_i's are NOT independent since $\sum_{i=1}^{c} x_i = 1$.

Therefore, we can express v in terms of any set of $c-1$ x_i's $\left[\begin{array}{l} V(T, P, N_1, N_2, \cdots N_c) \\ v(T, P, x_1, x_2, x_{c-1}) \end{array}\right]$

$$v = \sum_{i=1}^{c-1} x_i v_i + \underbrace{\left(1 - \sum_{i=1}^{c-1} x_i\right)}_{x_c} v_c$$

$$v = \sum_{i=1}^{c-1} x_i (v_i - v_c) + v_c$$

$$\Rightarrow \left(\frac{\partial v}{\partial x_i}\right)_{T,P,x_{j\neq 1,c}} = v_1 - v_c$$

$$\left(\frac{\partial v}{\partial x_2}\right)_{T,P,x_{j\neq 2,c}} = v_2 - v_c$$

$$\vdots \qquad\qquad \vdots$$

$$\left(\frac{\partial v}{\partial x_{c-1}}\right)_{T,P,x_{j\neq c-1,c}} = v_{c-1} - v_c$$

$$\sum_{i=1}^{c-1} x_i \left(\frac{\partial v}{\partial x_i}\right)_{T,P,x_{j\neq i,c}} = \sum_{i=1}^{c-1} x_i (v_i - v_c) = v - v_c x_c - v_c(1 - x_c)$$

$$= v - v_c$$

or

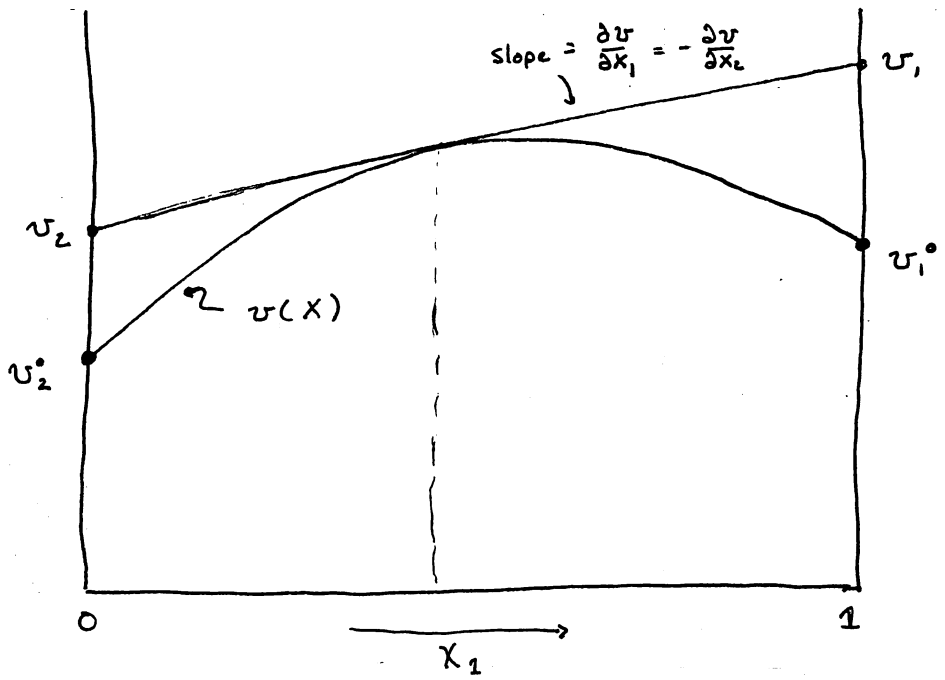
$$\boxed{v_c = v - \sum_{i=1}^{c-1} x_i \left(\frac{\partial v}{\partial x_i}\right)_{T,P,x_{j\neq i}}}$$

Thus, we can determine v_i for any component if $v(T,P,\underline{X})$ is known. (Note that v is only a function of C-1 composition variables)

Consider a 2-Component system:

$$v_2 = v - x_1 \left(\frac{\partial v}{\partial x_1}\right)_{T,P}$$

$$v_1 = v - x_2 \left(\frac{\partial v}{\partial x_2}\right)_{T,P} = v + x_2 \left(\frac{\partial v}{\partial x_1}\right)_{T,P}$$



III. Gibbs - Duhem Equation

For a single component phase it takes three variables to define the state of the system.

For Example, to uniquely define the state of water we can specify T, P, N. Note That we need to specify at least one Extensive variable so That we will know The size of The system.

However, once we specify only 2 intensive variables (i.e. T & P) Then all other intensive variables are fixed! The Gibbs - Duhem Equation provides us with a differential Equation relating the intensive variables of a homogeneous phase.

Recall Euler's Relation for a homogeneous phase:

$$U = TS - PV + \sum_{i=1}^{c} \mu_i N_i$$

$$dU = T dS + S dT - P dV - V dP + \sum_{i=1}^{c} \mu_i dN_i + \sum_{i=1}^{c} N_i d\mu_i$$

but, from the fundamental Equation,

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

so,

$$\Rightarrow \boxed{S dT - V dP + \sum_{i=1}^{c} N_i d\mu_i = 0}$$

Gibbs - Duhem Equation

Thus, for a homogeneous phase, The intensive parameters are not all independent but are related through the Gibbs-Duhem Equation.

Note for a Single Component phase:

$$N\,d\mu = -S\,dT + V\,dP$$

or

Single-component phase

$$\boxed{d\mu = -\Delta\,dT + v\,dP}$$

$\Delta \equiv S/N$

$v \equiv V/N$

More generally, for a multicomponent system:

$$\sum_{i=1}^{c} N_i\,d\mu_i = -S\,dT + V\,dP$$

or

$$\sum_{i=1}^{c} X_i\,d\mu_i = -\Delta\,dT + v\,dP$$

If T & P are fixed:

Restricted Gibbs-Duhem

$$\boxed{\sum_{i=1}^{c} X_i\,d\mu_i = 0}$$

single phase, fixed T & P.

We can generalize the restricted Gibbs-Duhem eqn. to any partial molar quantity

$V(T,P,\underline{N})$

$$dV = \sum_{i=1}^{c} v_i\,dN_i \qquad \text{fixed } T \text{ \& } P$$

$$V = \sum_{i=1}^{c} v_i N_i \qquad \text{always true}$$

$$dV = \sum_{i=1}^{c} v_i\,dN_i + \sum_{i=1}^{c} N_i\,dv_i \qquad \text{always true}$$

$$\Rightarrow \boxed{\begin{aligned} &\sum_{i=1}^{c} N_i\,dv_i = 0 \qquad \text{at fixed } T,P \\ \text{or}\quad &\sum_{i=1}^{c} X_i\,dv_i = 0 \end{aligned}}$$

Thus, all of the partial molar volumes in a multicomponent phase are not independent. For Example, in a 2-component phase:

$$dv_2 = -\frac{X_1\,dv_1}{X_2} = -\frac{X_1\,dv_1}{1-X_1}$$

A Similar Gibbs-Duhem Equation can be derived from the Massieu functions:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum \frac{\mu_i}{T} dN_i$$

and

$$S = \frac{1}{T}U + \frac{P}{T}V + \sum_{i=1}^{c} \frac{\mu_i}{T} N_i$$

$$\Rightarrow \boxed{U\, d\left(\frac{1}{T}\right) + V\, d\left(\frac{P}{T}\right) - \sum_{i=1}^{c} N_i\, d\left(\frac{\mu_i}{T}\right) = 0}$$

or

$$(U + PV)\, d\,{}^{1}\!/_{T} + \frac{V}{T} dP - \sum_{i=1}^{c} N_i\, d\left(\frac{\mu_i}{T}\right) = 0$$

$$\boxed{H\, d\left({}^{1}\!/_{T}\right) + {}^{V}\!/_{T}\, dP - \sum_{i=1}^{c} N_i\, d\left(\frac{\mu_i}{T}\right) = 0}$$

for a single component system:

$$\boxed{d\left(\frac{\mu}{T}\right) = h\, d\,{}^{1}\!/_{T} + \frac{v}{T} dP}$$

IV Maxwell Relations

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

$$\boxed{\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\underline{N}} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,\underline{N}'} \equiv -\Delta_i \qquad \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\underline{N}} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,\underline{N}'} \equiv v_i}$$

These 2 relations are extremely important and provide a useful scheme for determining the T & P dependence of the μ_i.

Note for a <u>single component system</u> Δ_i and v_i are molar quantities of pure substances (usually labelled Δ_i° and v_i°) instead of partral molar quantities. Also recall the Gibbs-Duhem Equation for a single component system:

$$d\mu = -\Delta dT + v\,dP \qquad \text{single-component}$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial T}\right)_P = -\Delta \quad ; \quad \left(\frac{\partial \mu}{\partial P}\right)_T = v$$

An important Maxwell relation involving the μ_i can also be obtained from the Massieu functions:

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

Legendre Transform: $$d\left[S - \frac{1}{T}U - \frac{P}{T}V\right] = -U\,d\frac{1}{T} - V\,d\frac{P}{T} - \sum \frac{\mu_i}{T} dN_i$$

or $$d\left(\frac{G}{T}\right) = U\,d\frac{1}{T} + V\,d\frac{P}{T} + \sum \frac{\mu_i}{T} dN_i$$

$$= (U + PV)\,d\frac{1}{T} + \frac{V}{T}dP + \sum \frac{\mu_i}{T} dN_i$$

$$\boxed{d\left(\frac{G}{T}\right) = H\,d\frac{1}{T} + \frac{V}{T}dP + \sum_{i=1}^{c} \mu_i/T\, dN_i}$$

$$\Rightarrow \boxed{\left(\frac{\partial\, \mu_i/T}{\partial\, 1/T}\right)_{P,\underline{N}} = \left(\frac{\partial H}{\partial N_i}\right)_{T,P,\underline{N}'} \equiv h_i}$$

Chemical Potentials - P, T & $\underline{x}$ dependence

Recall that knowledge of P, T, $\underline{x}$ dependence of the chemical potentials is central to the application of thermodynamics to chemical equilibrium problems.

For a single-component system, the chemical potential is simply the molar free energy:

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

or

$$\mu \equiv \bar{G} = \bar{u} - T\bar{s} + P\bar{v}$$

Single Component system

- molar volume → v or $\bar{v}$
- molar Entropy → s or $\bar{s}$
- molar Energy → u or $\bar{u}$

Absolute values of $\bar{v}$ and $\bar{s}$ (from the 3rd law) can be obtained. However, the absolute value of $\bar{u}$ is not meaningful. Only differences in $\bar{u}$ can be known, or the value of $\bar{u}$ relative to some reference state. Because the chemical potential contains $\bar{u}$, we can only know the value of μ relative to some reference state. This does NOT cause limitation. Regardless of what states we choose as our reference states, it is only differences in the μ_i which are important in chemical Thermodynamics.

It is important to emphasize that the choice of the standard state (reference state) is arbitrary. However, we must always keep in mind what the reference states are. The reference states are usually chosen out of CONVENIENCE. In fact, the reference state need NOT even be a real state!

For example, gaseous species are usually referenced to their hypothetical pure ideal-gas states. This is convenient because the pressure and composition dependence of the ideal gas state are simple functions and all gases follow ideal gas behavior in the limit of low densities.

For liquids & solids, the chemical potentials can also be referenced to the ideal gas state. Sometimes, however, it is more convenient to reference a liquid or solid component to a pure liquid or pure solid state. For solutes, we will find that it is most convenient to reference the chemical potential to a hypothetical "purely-dilute" state.

Before we go into the compositional dependences of chemical potentials we will first look at how we express the P & T dependence of μ for pure gases, liquids & solids.

Pure Gases - Ideal Gas Reference State

As mentioned, the chemical potential of real gases (and sometimes liquid and solids) are referenced to their ideal gas state. Thus, we first must know how to express the T & P dependence of μ for ideal gases.

$$\mu = \bar{u} - T\bar{s} + P\bar{v}$$
$$d\mu = d\bar{u} - T\,d\bar{s} - \bar{s}\,dT + P\,d\bar{v} + \bar{v}\,dP$$
$$d\mu = d\bar{u} - (d\bar{u}) + \bar{s}\,dT + \bar{v}\,dP$$
$$(\partial\mu/\partial P)_T = \bar{V}$$

recall, $\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} = v$ for any pure phase

$= \frac{RT}{P}$ for ideal gas, single-component

So, $d\mu = \bar{V}\,dP$

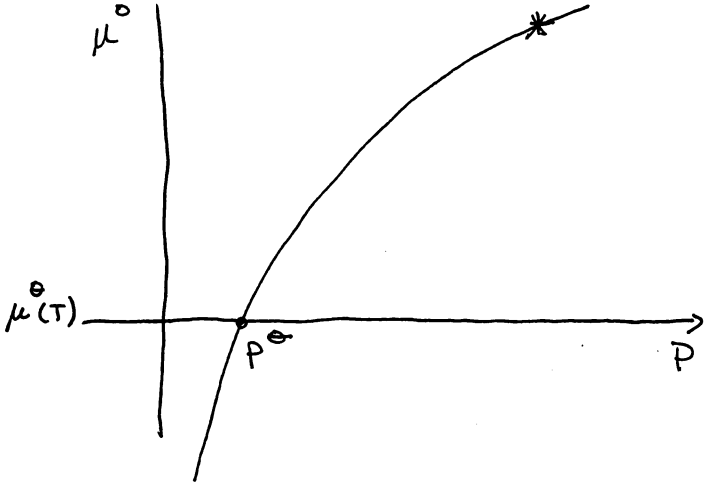
Now substitute in for $\bar{v}$ with the ideal EoS:

and Integrate

$$\underbrace{\mu^{\circ}(T,P)}_{\text{ideal gas chemical Potential}} = \mu^{\ominus}(T) + RT \ln P/P^{\ominus}$$

where $\mu^{\ominus}(T) \equiv$ ideal gas standard state @ T & $P = P^{\ominus}$ (standard Pressure)

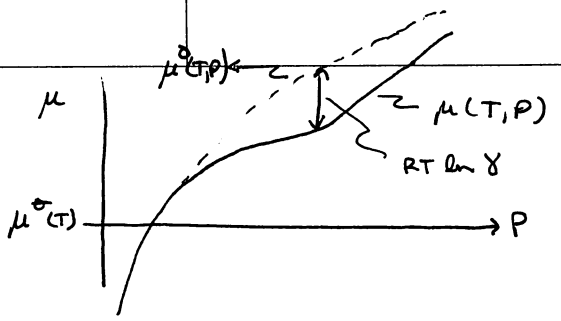
typically, the standard pressure, $P^{\ominus}$, is 1 bar but many older tables use a 1 atm reference state. Thus, it is important to know what the standard state is before you use the data



$$\mu^{\circ}(T,P_2) - \mu^{\circ}(T,P_1) = RT \ln \frac{P_2}{P_1}$$

all ideal gases have the same pressure dependence.

Real Gases - fugacity



Since all gases behave like ideal gases in the limit of low densities it is convenient to use the ideal gas state as the standard state for real gases.

$$\mu(T,P) \equiv \mu^{\ominus}(T) + RT \ln \frac{f(T,P)}{P^{\ominus}}$$

$\mu^{\ominus}(T)$ ← ideal gas reference at T & $P^{\ominus}$

$$f(T,P) \equiv P^{\ominus} e^{\frac{\mu-\mu^{\ominus}}{RT}}$$

$f(T,P)$ ≡ "fugacity"

The "fugacity" has units of pressure. It's value can be greater or less than the actual pressure. The fugacity is a measure of the "escaping tendency" of the gas.

if $f < P$ attraction between molecules "negative deviation from ideality"

if $f > P$ repulsion between molecules "positive deviation from ideality"

$\lim_{P \to 0} f \longrightarrow P$

The fugacity equals the pressure (ideal) in the limit of $P \to 0$.

Fugacity Coefficient, $\gamma(T,P)$

By definition

$$\gamma(T,P) \equiv \frac{f(T,P)}{P}$$

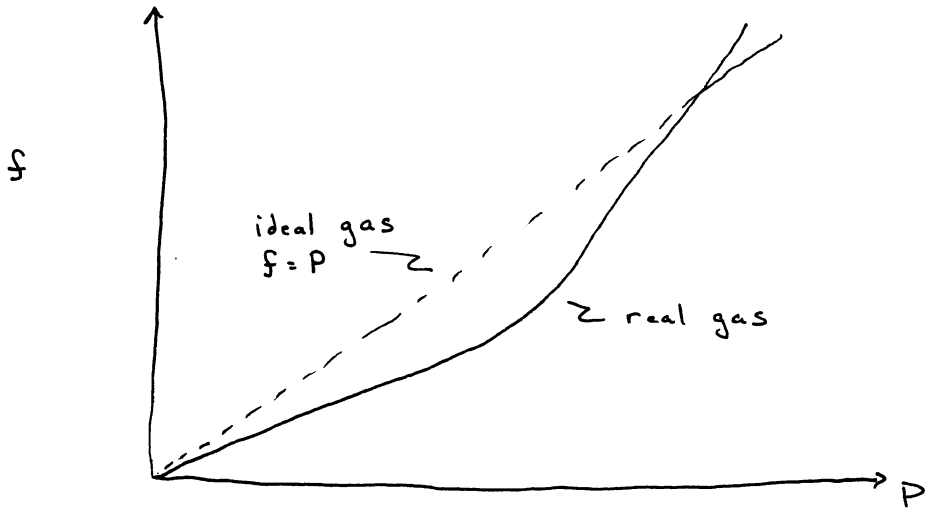
The fugacity coefficient is a unitless number.

$$\lim_{P \to 0} \gamma(T,P) \to 1$$

Therefore, we can write for $\mu(T,P)$:

$$\mu(T,P) = \mu^{\theta}(T) + RT \ln \frac{f(T,P)}{P^{\theta}}$$

$$= \underbrace{\mu^{\theta}(T) + RT \ln \frac{P}{P^{\theta}}}_{\mu^{0}(T,P)\ \text{ideal gas}} + RT \ln \gamma(T,P)$$



One way to view the fugacity is that it represents the pressure that an ideal gas would have to have in order to have the same escaping tendency as the real gas.

Pure liquids and Solids - single component systems

Since there is NO reference model ideal Equation of state for liquids or solids, we typically reference the chemical potential of a condensed phase to that of its pure liquid or solid at $P = P^\ominus$ and at the temperature of interest.

Recall, $\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V}(T,P) = v(T,P)$

$$\Rightarrow \mu^\bullet(T,P) = \mu^\bullet(T,P^\ominus) + \underbrace{\int_{P^\ominus}^{P} \bar{V}^\bullet \, dP}_{\approx \bar{V}^\bullet (P - P^\ominus)}$$

The filled circle ($\bullet$) indicates pure liquid or solid phases.

It is often convenient to reference the chemical potential of a condensed phase to that of its ideal gas state. In this way we *define* the fugacity of a liquid or solid in the same way as we did for a gas:

$$\mu^\bullet(T,P) = \underbrace{\mu^\ominus(T)}_{\text{ideal gas reference state at } P^\ominus} + RT \ln \frac{f^\bullet(T,P)}{P^\ominus}$$

The fugacity represents the pressure that an ideal gas would have if it were in chemical Equilibrium with the condensed phase. The solid ($\bullet$) is a reminder that this is the fugacity of a pure liquid or solid.

Fugacity as an "Escaping tendency"

Consider a sample of water contained at T & P. Now, suppose the water is in chemical Equilibrium with its vapor through a "Gore-Tex" membrane, i.e., only the vapor can be transported through the membrane.

T, P	T, P^{vap}
liquid	vapor

at Equilibrium,

$$\boxed{\mu^{\bullet,\ell}(T,P) = \mu^{g}(T,P^{vap})}$$

$$\Rightarrow \mu^{\bullet}(T) + RT \ln \frac{f^{\bullet,\ell}(T,P)}{P^{\bullet}} = \mu^{\bullet}(T) + RT \ln \frac{f^{g}(T,P^{vap})}{P^{\bullet}}$$

$$\Rightarrow \boxed{f^{\bullet,\ell}(T,P) = f^{g}(T,P^{vap})}$$

an alternative criteria for Chemical Equilibrium

Therefore, the fugacity can truly be thought of as an "Escaping tendency". At Equilibrium, the fugacity of a component is the same in each of the phases.

Also, the above relations show that, like the chemical potential, we can use fugacity as a measure of Equilibrium.

As with gases, we can <u>define</u> the fugacity Coefficient γ as:

$$\gamma(T,P) \equiv \frac{f(T,P)}{P}$$

Pressure Dependence of γ (pure liquids, solids, or gases)

Recall, $\mu(T,P) = \mu^{\ominus}(T) + RT \ln \frac{f(T,P)}{P^{\ominus}}$

$= \mu^{\ominus}(T) + RT \ln \frac{P}{P^{\ominus}} + RT \ln \gamma(T,P)$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} = \frac{RT}{P} + RT \left(\frac{\partial \ln \gamma}{\partial P}\right)_T$$

or

$$\left(\frac{\partial \ln \gamma}{\partial P}\right)_T = \frac{\bar{V} - \bar{V}^{\circ}}{RT}$$

where $\bar{V}^{\circ} \equiv$ ideal gas volume at T, P.

$$\Rightarrow \int_{\ln \gamma(P=0,T)}^{\ln \gamma(P,T)} d \ln \gamma = \int_0^P \frac{\bar{V} - \bar{V}^{\circ}}{RT} dP \qquad \text{fixed } T$$

$$\ln \gamma(P,T) - \ln \gamma(P=0,T) = \int_0^P \frac{\bar{V} - \bar{V}^{\circ}}{RT} dP$$

$\ln \gamma(P=0,T) \to 0$, since all gases are ideal in the limit of $P = 0$

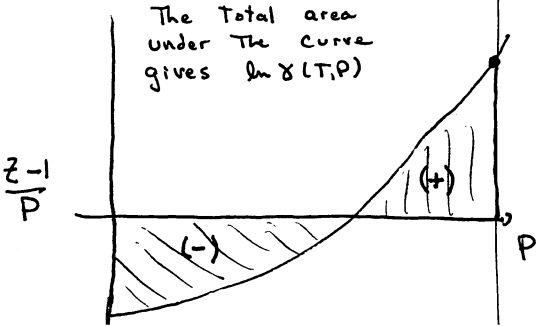
Thus, if we know $\bar{V} - \bar{V}^{\circ}$ as a function of P for the gas, we can determine $\gamma(P,T)$.

If the equation of state of the gas is expressed as a virial expansion then we can write:

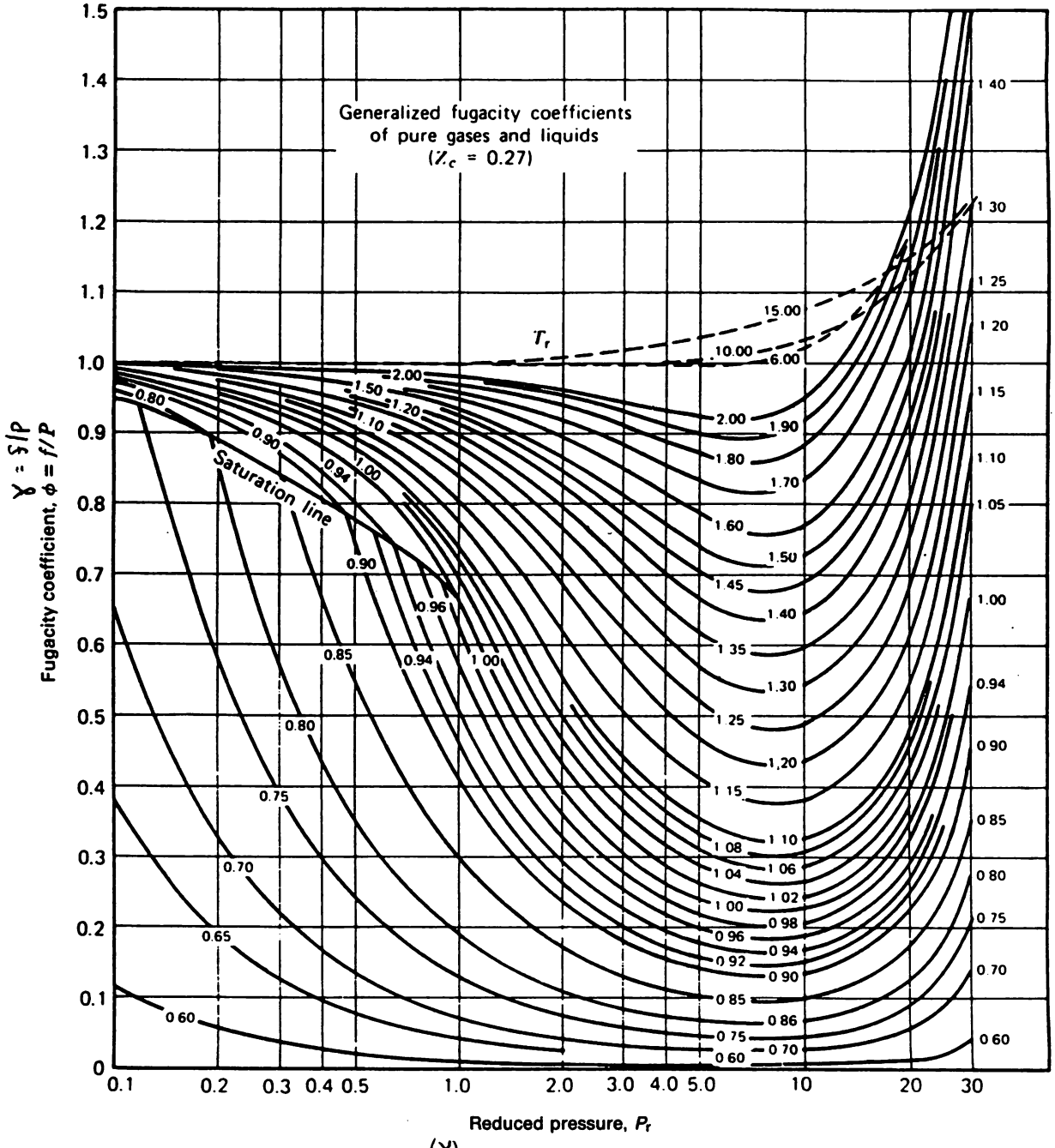
$$Z = 1 + \frac{B'}{RT} P + \frac{C'}{RT} P^2 + \cdots$$

$$\boxed{\ln \gamma(T,P) = \int_0^P \frac{Z-1}{P'} dP'} = \int_0^P \frac{B'}{RT} + \frac{C'}{RT} P + \cdots dP'$$

$$= \frac{B'P}{RT} + \frac{C'P^2}{2RT} + \frac{D'P^3}{3RT} + \cdots$$



$\frac{Z-1}{P}$



Fugacity coefficient ϕ as a function of reduced pressure P_r and reduced temperature T_r. (From O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles Charts*, 2d ed. New York: Wiley, 1960.)

Ideal Gas Mixtures

Recall that for the ideal gas model, there are NO intermolecular interactions. Thus, the molecules act completely independently. In the ideal gas model, the total internal energy of the system, u, can be simply expressed as a sum over the energy of each molecule.

An ideal gas mixture has the following properties,

① $V = \frac{RT}{P} \sum_{i=1}^{c} N_i \Rightarrow \Delta_{mix} V\,(T,P,\underline{N}) = 0$

② $\left(\frac{\partial u}{\partial V}\right)_{T,\underline{N}} = 0$

③ $u = u(T,\underline{N}) = \sum_{i=1}^{c} N_i \bar{u}_i^{\circ}(T) \Rightarrow \Delta_{mix} u\,(T,P,\underline{N}) = 0$

also from ① & ③

$$H = H(T,\underline{N}) = \sum_{i=1}^{c} N_i \bar{H}_i^{\circ}(T) \Rightarrow \Delta_{mix} H\,(T,P,\underline{N}) = 0$$

④ In the ideal model, the $\Delta_{mix} S\,(T,P,\underline{N})$ is given solely by the ideal configurational entropy of mixing.

$$\Delta_{mix} S\,(T,P,\underline{N}) = -\sum_{i=1}^{c} N_i R \ln y_i$$

(y_i is the mole fraction of the i^{th} species in vapour phase, x_i = condensed phase)

These properties of an ideal gas mixture are obeyed only if the chemical potentials of the ideal gas components are given by:

$$\mu_i(T,P,\underline{y}) = \mu_i^{\circ}(T,P) + RT \ln y_i$$

$$= \mu_i^{\ominus}(T) + RT \ln \frac{P y_i}{P^{\ominus}}$$

$$\boxed{\mu_i(T,P,\underline{y}) = \mu_i^{\ominus}(T) + RT \ln \frac{p_i}{P^{\ominus}}}$$

where $p_i \equiv P y_i \Rightarrow$ The fugacity of an ideal gas is its partial pressure.

This Equation defines what we mean by the "partial pressure" regardless of a real or ideal gas.

To evaluate the mixing quantities of ideal gases, consider:

$$\Delta_{mix} H(T,P,\underline{N}) \equiv H(T,P,N) - \sum_{i=1}^{c} N_i \bar{H}_i^{\circ}(T,P)$$

$$= \sum_{i=1}^{c} N_i \left[\bar{H}_i(T,P,\underline{y}) - \bar{H}_i^{\circ}(T,P) \right]$$

Recall, from the definition,

$$\mu_i(T,P,\underline{y}) = \mu_i^{\circ}(T,P) + RT \ln y_i$$

$$\left(\frac{\partial \mu_i/T}{\partial 1/T} \right)_{P,N} = \bar{H}_i(T,P,y) = \bar{H}_i^{\circ}(T,P)$$

$$\boxed{\Delta_{mix} H(T,P,\underline{N}) = 0}$$

$$\Delta_{mix} V(T,P,\underline{N}) \equiv \sum_{i=1}^{c} N_i \left[\bar{V}_i(T,P,\underline{y}) - \bar{V}_i^{\circ}(T,P) \right]$$

from, $\mu_i(T,P,\underline{y}) = \mu_i^{\circ}(T,P) + RT \ln y_i$

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T,\underline{N}} = \bar{V}_i(T,P,\underline{y}) = \bar{V}_i^{\circ}(T,P)$$

$$\Rightarrow \quad \boxed{\Delta_{mix} V(T,P,\underline{N}) = 0}$$

$$\Delta_{mix} u(T,P,\underline{N}) \equiv \Delta_{mix} H - P \Delta_{mix} V$$

($\Delta_{mix} H = 0$, $\Delta_{mix} V = 0$)

$$\boxed{\Delta_{mix} u(T,P,\underline{N}) = 0}$$

$$\Delta_{mix} S(T,P,\underline{N}) \equiv \sum_{i=1}^{c} N_i \left[\bar{S}_i(T,P,\underline{y}) - \bar{S}_i^{\circ}(T,P) \right]$$

again from: $\mu_i(T,P,\underline{y}) = \mu_i^{\circ}(T,P) + RT \ln y_i$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\bar{S}_i(T,P,y) = -\bar{S}_i^{\circ}(T,P) + R \ln y_i$$

$$\Rightarrow \quad \bar{S}_i(T,P,y) - \bar{S}_i^{\circ}(T,P) = -R \ln y_i$$

or

$$\boxed{\Delta_{mix} S\,(T,P,\underline{N}) = -\sum_{i=1}^{c} N_i R \ln y_i}$$

The Entropy of mixing of ideal gases is solely given by the complete configurational contribution, i.e., completely random.

Alternately, we can start with G and derive μ_i for gas mixtures:

$$\Delta_{mix} G\,(T,P,\underline{N}) = \Delta_{mix} H\,(T,P,\underline{N}) - T\,\Delta_{mix} S\,(T,P,\underline{N})$$

($\Delta_{mix} H = 0$)

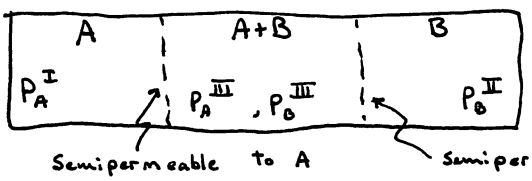
(valid for ideal gas model)

$$\boxed{\begin{aligned}\Delta_{mix} G(T,P,\underline{N}) &= RT \sum_{i=1}^{c} N_i \ln y_i \\ &= NRT \sum_{i=1}^{c} y_i \ln y_i\end{aligned}}$$

Thus, our model for the chemical potential of ideal gases in a mixture is consistent with all of the expected properties of an ideal gas.

Dalton's Law (only valid for ideal gas mixtures)

Consider the following composite system:



@ Equilibrium $\mu_A^I(T, P_A^I) = \mu_A^{III}(T, P, y)$

$$\Rightarrow \mu_A^{\ominus}(T) + RT \ln \frac{P_A^I}{P^{\ominus}} = \mu_A^{\ominus}(T) + RT \ln \frac{P_A^{III}}{P^{\ominus}}$$

$$\Rightarrow P_A^I = P_A^{III} \qquad P^{III} = P_A^I + P_B^{II}$$

also, $P_B^{II} = P_B^{III}$

Real Gas Mixtures

(replace partial pressures with fugacities)

For real gas mixtures we can write the chemical potential, μ_i, as:

$$\mu_i(T,P,\underline{y}) = \mu_i^{\ominus}(T) + RT \ln \frac{f_i(T,P,\underline{y})}{P^{\ominus}}$$

$$\lim_{P\to 0} f_i \to P_i$$

Note: in the limit the total $P \to 0$, NOT just P_i!

Define:

$$\gamma_i(T,P,\underline{y}) \equiv \frac{f_i(T,P,\underline{y})}{P_i} = \frac{f_i(T,P,\underline{y})}{P\,y_i}$$

$$\lim_{P\to 0} \gamma_i \to 1$$

$$\Rightarrow \mu_i(T,P,\underline{y}) = \mu_i^{\ominus}(T) + RT \ln \frac{P_i}{P^{\ominus}} + RT \ln \gamma_i(T,P,\underline{y})$$

alternatively, Since $P_i = P y_i$ we can write:

$$\mu_i(T,P,\underline{y}) = \underbrace{\mu_i^{\ominus}(T) + RT \ln \frac{P}{P^{\ominus}}}_{\mu_i^{\circ}(T,P)\ \text{ideal gas @ } T,P} + RT \ln y_i \gamma_i$$

$\gamma_i(T,P,\underline{y})$ for real gas mixtures can be found in an analogous way to that of pure gases:

$$\ln y_i \gamma_i = \frac{\mu_i(T,P,\underline{y}) - \mu_i^{\circ}(T,P)}{RT}$$

Now taking a derivative with respect to P at fixed T & $\underline{N}$,

$$\Rightarrow \left(\frac{\partial \ln \gamma_i(T,P,\underline{y})}{\partial P}\right)_{T,\underline{N}} = \frac{\bar{V}_i(T,P,\underline{y}) - \bar{V}_i^{\circ}}{RT}$$

[Note: $\left(\frac{\partial \ln y_i}{\partial P}\right)_{T,\underline{N}} = 0$]

$$\Rightarrow \quad \ln \gamma_i (T,P,\underline{y}) = \int_0^P \frac{\bar{V}_i(T,P,\underline{y}) - \bar{V}_i^\circ}{RT} \, dP'$$

[$\ln \gamma_i (T, P=0, \underline{y}) = 0$]

$$\ln \gamma_i (P,T,\underline{y}) = \int_0^P \frac{Z_i (T,P,\underline{y}) - 1}{P} \, dP'$$

In principle, to extract γ_i as a function of $T, P, \& \underline{y}$ we would have to know $\bar{V}_i (T,P,\underline{y})$. This data is typically only known for a few important mixtures.

$$Z_i \equiv \frac{P\bar{V}_i}{RT}$$

Often we use an approximation developed by Lewis & Randall.

Gilbert Lewis and Merle Randall, "Thermodynamics", McGraw-Hill Book Company (1961).

Lewis & Randall Approximation

$$f_i(T,P,\underline{y}) \cong f_i^{\bullet}(T,P)\, y_i$$

where $f_i^{\bullet}(T,P)$ is the fugacity of the pure component at the same total pressure, P, of the mixture

With this approximation, the chemical potential can also be written:

$$\mu_i(T,P,\underline{y}) = \mu_i^{\ominus}(T) + RT \ln \frac{f_i^{\bullet}(T,P)\, y_i}{P^{\ominus}}$$

$$= \mu_i^{\ominus}(T) + RT \ln \frac{f_i^{\bullet}(T,P)}{P^{\ominus}} + RT \ln y_i$$

$$= \underbrace{\mu_i^{\bullet}(T,P)}_{\text{pure real gas}} + RT \ln y_i$$

$$\left[\mu_i^{\bullet}(T,P) = \mu_i^{\circ}(T,P) + RT \ln \gamma\right]$$

The Lewis & Randall approximation is tantamount to assuming that:

$$\gamma_i(T,P,\underline{y}) \approx \gamma_i^{\bullet}(T,P)$$

proof:

$$f_i \equiv P_i \gamma_i = P y_i \gamma_i = P \gamma_i^{\bullet}\, y_i \frac{\gamma_i}{\gamma_i^{\bullet}}$$

$$f_i = f_i^{\bullet}\, y_i \frac{\gamma_i}{\gamma_i^{\bullet}} \approx f_i^{\bullet}\, y_i \quad \text{if} \quad \gamma_i \approx \gamma_i^{\bullet} \quad \therefore$$

Pressure Dependence of γ - Revisited (pure liquids, solids, or gases)

Recall, $\mu(T,P) = \mu^{\ominus}(T) + RT \ln \frac{f(T,P)}{P^{\ominus}}$

$= \mu^{\ominus}(T) + RT \ln \frac{P}{P^{\ominus}} + RT \ln \gamma(T,P)$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} = \frac{RT}{P} + RT \left(\frac{\partial \ln \gamma}{\partial P}\right)_T$$

or

$$\left(\frac{\partial \ln \gamma}{\partial P}\right)_T = \frac{\bar{V} - \bar{V}^{\circ}}{RT}$$

where $\bar{V}^{\circ} \equiv$ ideal gas volume at T, P.

$$\Rightarrow \int_{\ln\gamma(P=0,T)}^{\ln\gamma(P,T)} d \ln \gamma = \int_0^P \frac{\bar{V} - \bar{V}^{\circ}}{RT} dP \qquad \text{fixed } T$$

$$\ln \gamma(P,T) - \cancel{\ln \gamma(P=0,T)} = \int_0^P \frac{\bar{V} - \bar{V}^{\circ}}{RT} P$$

0 (since all gases are ideal in the limit of $P \to 0$)

Thus, if we know $\bar{V} - \bar{V}^{\circ}$ as a function of P for the gas, we can determine $\gamma(P,T)$

$$\ln \gamma(P,T) = \int_0^P \left(\frac{P\bar{V}}{RT} - \frac{P\bar{V}^{\circ}}{RT} \right) \frac{dP}{P} = \int_0^P \frac{Z - 1}{P'} dP'$$

$Z \equiv \frac{PV}{RT}$ compressibility factor ($= 1$ for ideal gas)

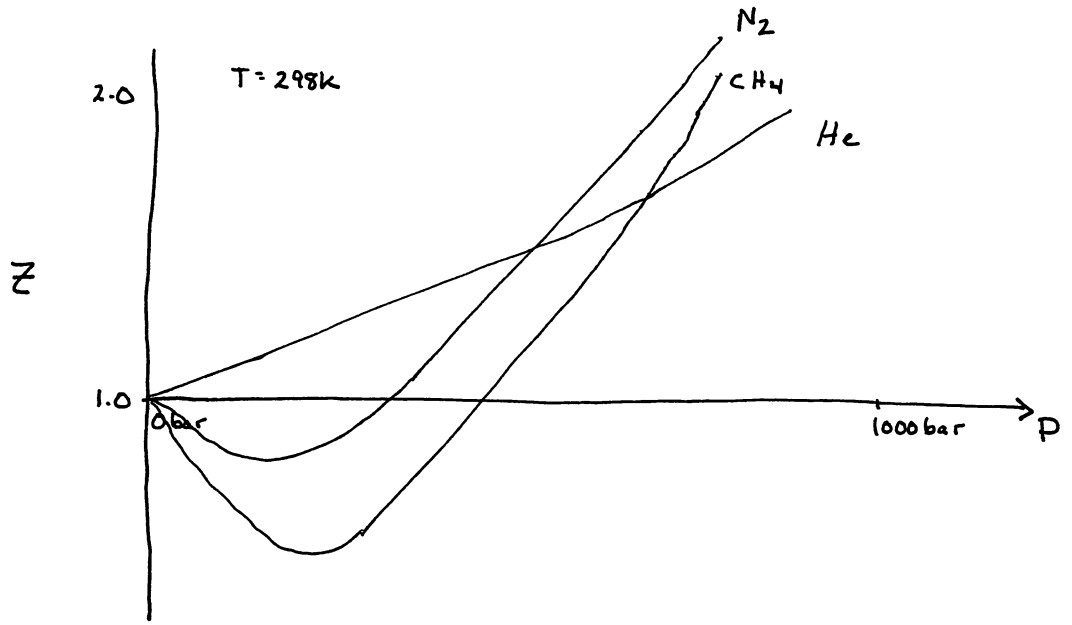
Several other important EoS's of gases are based on expansions of the compressibility factor.

Real Gases : Compressibility Factor, Z

Real gases only behave ideally in the limit of low pressure. A convenient measure of the deviation in ideality of a real gas is given by the "compressibility factor", Z

$$Z = \frac{P\bar{V}}{RT}$$

Compressibility factor



All gases show a minimum in $Z(P)$ *if* the temperature is low Enough. Deviation of $Z < 1$ at low T & P are generally due to attractive forces. At high pressure (high densities) repulsive forces increase $Z > 1$

Several important EoS's are written as power series Expansions of Z.

Virial Expansions

A useful analytical form for the equation of state of a gas or liquid is the "virial Expansion". The virial Expansion is based on a power series expansion of the compressibility factor, z, in terms of $(1/\bar{v})$ or P.

$(1/\bar{v})$ virial Expansion:

$$z(P,T) = z_0 + \frac{\left(\frac{\partial z}{\partial 1/\bar{v}}\right)_T}{1!}\bigg|_{P=0}\left(\frac{1}{\bar{v}}\right) + \frac{\left(\frac{\partial^2 z}{\partial 1/\bar{v}^2}\right)_T}{2!}\bigg|_{P=0}\left(\frac{1}{\bar{v}^2}\right) + \cdots$$

$$\boxed{z = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \cdots}$$

where $B(T) \equiv$ Second virial Coefficient
$C(T) \equiv$ Third virial Coefficient

$z_0 = 1$ value of z in the limit of $P \to 0$

Pressure virial Expansion:

$$z(T,P) = z_0 + \left(\frac{\partial z}{\partial P}\right)_T\bigg|_{P=0} P + \frac{1}{2!}\left(\frac{\partial^2 z}{\partial P^2}\right)_T\bigg|_{P=0} P^2 + \cdots$$

$$\boxed{z = 1 + B'(T)P + C'(T)P^2 + \cdots}$$

Relation between B', C' and B, C:

$$z = \frac{P\bar{v}}{RT} = 1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \cdots$$

Now, Solving for P & keeping terms To $\frac{1}{\bar{v}^2}$,

$$P = \frac{RT}{\bar{v}} + \frac{RTB}{\bar{v}^2} + \cdots$$

Substitute into P - virial Expansion:

$$z = 1 + \frac{B'RT}{\bar{v}} + \left(C'(RT)^2 + BB'RT\right)\frac{1}{\bar{v}^2} + \cdots$$

$$\boxed{\begin{aligned} B &= B'RT & B' &= B/RT \\ C &= (C' + B'^2)R^2T^2 & C' &= C - B^2/R^2T^2 \end{aligned}}$$

Pure liquids & Solids - revisited

Review p. 191 of Notes:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V}(T,P)$$

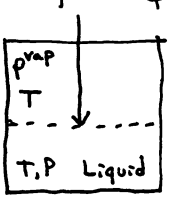
$$\boxed{\mu^\circ(T,P) = \mu^\circ(T,P^\theta) + \underbrace{\int_{P^\theta}^{P} \bar{V}^\circ dP}_{\approx \bar{V}^\circ (P-P^\theta)}}$$

$$\mu^\circ(T,P) = \mu^\theta(T) + RT \ln \frac{f^\circ(T,P)}{P^\theta}$$

Thus, by definition, the fugacity of a pure liquid or solid at T & P is given by:

$$\boxed{\ln \frac{f^\circ(T,P)}{P^\theta} = \frac{\mu^\circ(T,P) - \mu^\theta(T)}{RT}}$$

Lets investigate the physical meaning of this fugacity. Consider the Equilibration of some pure liquid at T, P with its vapor where the vapor pressure, P^{vap}, is not necessarily the same as that of pressure on the liquid.



@ Equilibrium:

$$\mu^{\circ,\ell}(T,P) = \mu^g(T,P^{vap})$$

$$\Rightarrow \mu^\theta(T) + RT \ln \frac{f^{\circ,\ell}(T,P)}{P^\theta} = \mu^\theta(T) + RT \ln \frac{f^g(T,P^{vap})}{P^\theta}$$

also @ Equilibrium $\boxed{f^{\circ,\ell}(T,P) = f^g(T,P^{vap})}$

> Therefore, the fugacity can truly be thought of as the "Escaping tendency". At Equilibrium, the fugacity of a Component is the same in each of the phases.

Thus, in addition to using chemical potentials as a measure of Equilibrium we can alternatively use fugacity as a measure of Equilibrium!

A convenient method to obtain the fugacity of a liquid or solid is to reference it back to data we have available in the thermochemical tables at $P^\ominus$. For example:

$$\ln \frac{f^\circ(T,P)}{P^\ominus} = \ln \frac{f^\circ(T,P)}{f^\circ(T',P^\ominus)} + \ln \frac{f^\circ(T',P^\ominus)}{P^\ominus}$$

The second term is simply the fugacity at $P^\ominus$ and at any reference temperature, T'.

$$\ln \frac{f^\circ(T',P^\ominus)}{P^\ominus} = \frac{\mu^\circ(T',P^\ominus) - \mu^\ominus(T')}{RT'}$$

$$= -\frac{\Delta G^\ominus(T')}{RT'}$$

It is important to note, however, that $\Delta G^\ominus$ here is <u>not</u> the actual ΔG_{vap} or ΔG_{sub} of the liquid or solid, but simply the free energy difference between either the liquid at $P^\ominus, T'$ and its ideal gas reference state at $P^\ominus, T'$ or the solid at $P^\ominus, T'$ and its ideal gas reference state at $P^\ominus, T'$.

Sometimes a more convenient reference point would be some point along the equilibrium saturation line, i.e., either along the sublimation or vaporization lines. Along these lines we know that the fugacity of the liquid (or solid) is equal to the fugacity of the vapor.

i.e.,

$$\ln \frac{f^\circ(T,P)}{P^\ominus} = \ln \frac{f^\circ(T,P)}{f^\circ(T^{sat},P^{sat})} + \underbrace{\ln \frac{f^\circ(T^{sat},P^{sat})}{P^\ominus}}_{\ln \frac{f^g(T^{sat},P^{sat})}{P^\ominus}}$$

To a very good approximation,

$$f^{g}(T^{sat}, p^{sat}) \approx p^{sat}$$

The saturation vapor pressure

For more exact calculations we would need to know the fugacity coefficient of the gas at p^{sat}, T^{sat}.

In either case above we still need to know how to calculate the P, T dependence of f° for a pure phase.

Pressure Dependence of Fugacity - General treatment

whether we are talking about a solid, liquid, or gas, The fugacity of a pure component in any phase is defined by:

$$\ln f^{\bullet}(T,P) = \frac{\mu^{\bullet}(T,P) - \mu_i^{\ominus}(T)}{RT}$$

The isothermal pressure dependence of $\ln f$ is given by:

$$\left(\frac{\partial \ln f^{\bullet}}{\partial P}\right)_T = \frac{\left(\frac{\partial \mu^{\bullet}}{\partial P}\right)_T - \left(\frac{\partial \mu_i^{\ominus}(T)}{\partial P}\right)_T}{RT} \quad \left(\frac{\partial \mu_i^{\ominus}(T)}{\partial P} \to 0\right)$$

$$\boxed{\left(\frac{\partial \ln f^{\bullet}}{\partial P}\right)_T = \frac{v^{\bullet}}{RT} = \frac{\bar{V}^{\bullet}}{RT}}$$

Generally true for any pure phase.

Thus, we must know $v(T,P)$ to obtain the pressure dependence of f.

$$\ln f^{\bullet}(T,P) = \ln f^{\bullet}(T,P^{\ominus}) + \int_{P^{\ominus}}^{P} \frac{v^{\bullet}(T,P)}{RT}\, dP$$

If the pressure range is not very large, to a first approximation we can treat a liquid or solid as incompressible. In This way we can approximate:

$$\ln f^{\bullet}(T,P) \cong \ln f^{\bullet}(T,P^{\ominus}) + \frac{v^{\bullet}(T,P^{\ominus})}{RT}(P - P^{\ominus})$$

more exactly we must include the P dependence of v. Typically, however, E.o.S data is given as $P(T,v)$ instead of $v(T,P)$. For this reason it is sometimes more convenient To integrate over v rather than P.

recall, $v\,dP = d(Pv) - P\,dv$

$$\Rightarrow \ln f^{\bullet}(T,P) = \ln f^{\bullet}(T,P^{\ominus}) + Pv(T,P) - P^{\ominus}v^{\ominus} - \int_{v^{\ominus}}^{v(P)} P\,dv$$

Temperature Dependance of Fugacity - General Treatment

Recall, for a pure phase

$$\left(\frac{\partial\, \mu^\circ/T}{\partial\, 1/T}\right)_P = \mathcal{H}^\circ(T,P)$$

Note:
$$dS = \frac{1}{T}dH - \frac{V}{T}dP - \frac{\mu}{T}dN$$
$$dS\left[\frac{1}{T}\right] = -H\,d\frac{1}{T} - \frac{V}{T}dP - \frac{\mu}{T}dN$$

where $\mathcal{H}^\circ \equiv$ molar Enthalpy

$$\frac{\ln f^\circ(T,P)}{P^\theta} \equiv \frac{\mu^\circ(T,P) - \mu^\theta(T)}{RT}$$

$$\left(\frac{\partial \ln f^\circ}{\partial\, 1/T}\right)_P = \frac{\mathcal{H}^\circ(T,P) - \mathcal{H}^\theta(T)}{R}$$

or

$$\left(\frac{\partial \ln f^\circ}{\partial T}\right)_P = \frac{\mathcal{H}^\theta(T) - \mathcal{H}^\circ(T,P)}{RT^2}$$

Thus, to obtain the temp. dependence of f°, we must know the Enthalpy difference between the pure phase of interest and that of its ideal gas reference state.

For gases, This difference is typically very small and only reflects the non-ideality of the gas. However, for liquids and solids This difference is on the order of The heat of vaporization or sublimation.

Summary for Gases

① Ideal gas mixtures:

$$\mu_i(T,P,y) = \mu_i^{\circ}(T,P) + RT \ln y_i$$

$$= \mu_i^{\ominus}(T) + RT \ln P/P^{\ominus} + RT \ln y_i$$

$$= \mu_i^{\ominus}(T) + RT \ln P_i/P^{\ominus}$$

where $P_i \equiv P y_i$

② Real gas mixtures:

$$\mu_i(T,P,y) = \mu_i^{\ominus}(T) + RT \ln \frac{f_i(T,P,\underline{y})}{P^{\ominus}}$$

$$= \mu_i^{\ominus}(T) + RT \ln P_i/P^{\ominus} + RT \ln \gamma_i(T,P,\underline{y})$$

$$= \mu_i^{\ominus}(T) + RT \ln P/P^{\ominus} + RT \ln y_i \gamma_i(T,P,\underline{y})$$

$$= \mu_i^{\circ}(T,P) + RT \ln y_i \gamma_i(T,P,\underline{y})$$

where $\left.\begin{array}{l} f_i \to P_i \\ \& \\ \gamma_i \to 1 \end{array}\right\}$ in Lim $P \to 0$

③ Lewis & Randall Approximation:

$$f_i = f_i^{\bullet} y_i$$

$$\mu_i(T,P,y) \approx \mu_i^{\circ}(T) + RT \ln f_i^{\bullet}/P^{\ominus} + RT \ln y_i$$

$$= \mu_i^{\bullet}(T,P) + RT \ln y_i$$

Activities

Before beginning our application of chemical potentials to chemical Equilibrium problems, its important to mention one very general way to express the chemical potential:

For any component, in any phase we can generally write:

$$\boxed{\mu_i(T,P,\underline{x}) = \mu_i^*(T,P) + RT \ln a_i(T,P,\underline{x})}$$

μ_i^* is some reference state chemical potential and $a_i(T,P,\underline{x})$ is a unitless number called The activity.

The activity can be related to the fugacity.

$$RT \ln a_i(T,P,\underline{x}) = \mu_i(T,P,\underline{x}) - \mu_i^*(T,P)$$

we can also write:

$$\mu_i(T,P,\underline{x}) = \mu_i^{\ominus}(T) + RT \ln \frac{f_i(T,P,\underline{x})}{P^{\ominus}}$$

;

$$\mu_i^*(T,P) = \mu_i^{\ominus}(T) + RT \ln \frac{f_i^*(T,P)}{P^{\ominus}}$$

$$\ln a_i(T,P,\underline{x}) = \ln \frac{f_i}{P^{\ominus}} - \ln \frac{f_i^*}{P^{\ominus}}$$

$$\Rightarrow \boxed{a_i(T,P,\underline{x}) = \frac{f_i(T,P,\underline{x})}{f_i^*(T,P)}}$$

Ratio of the actual fugacity and the fugacity of the standard state.

This is a general definition of activity.

Chemical Equilibrium

General Treatment :

Recall that a balanced chemical reaction can be represented by the algebraic Equation : (p36)

$$\sum_{i=1}^{s} \nu_i A_i = 0$$

where $A_i \equiv$ chemical species

$\nu_i \equiv$ stoichiometric coefficient $\begin{cases} \nu > 0 & \text{products} \\ \nu < 0 & \text{reactants} \end{cases}$

and the sum is over all of the chemical species, s, involved in the reaction.

We will first consider a system in which a single reaction occurs in a single phase.

At fixed T & P the final Equilibrium state is that state which minimizes the Gibbs Free Energy of the system.

The change in the Gibbs Energy due to changes in the abundances of the species involved in the reaction is given by :

$$dG = \sum_{i=1}^{s} \mu_i \, dN_i \qquad \text{for fixed } T \& P$$

Assuming that the system is closed and that N_i can only change due to a change in the extent of the reaction, we can write:

$$dN_i = \nu_i \, d\xi \qquad \text{for closed system and single reaction}$$

where $\xi \equiv$ Extent of reaction

$$N_i(\xi) = N_{i,0} + \nu_i \xi$$

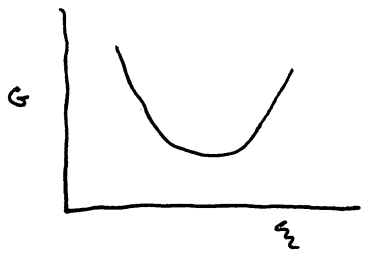
N_{i0} is the initial concentration of species i

$$\Rightarrow dG = \left(\sum_{i=1}^{s} \nu_i \mu_i \right) d\xi$$

Single reaction at fixed T,P in closed system.

At Equilibrium the Gibbs Free Energy is a minimum for a system at fixed T & P. The minimum value of G occurs where

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$$



fixed T & P

$$\sum_{i=1}^{s} \nu_i \mu_i = 0$$

or

$$\Delta_r G = 0$$

Equilibrium Condition

$$\Delta_r G\,(T,P,\underline{x}) \equiv \sum_{i=1}^{s} \nu_i \mu_i\,(T,P,\underline{x})$$

The most general form for the chemical potential is given by:

$$\mu_i\,(T,P,\underline{x}) = \mu_i^*\,(T) + RT \ln a_i\,(T,P,\underline{x})$$

μ_i^* reference state could be either at standard pressure, $P^\ominus$, or at the pressure, P. The value of a_i will reflect which standard state is used.

where $a_i(T,P,\underline{x}) \equiv \dfrac{f_i(T,P,\underline{x})}{f_i^*(T,P)}$

Substituting $\mu_i(T,P,\underline{x})$ into $\Delta_r G$ we have:

$$\Delta_r G = \sum_{i=1}^{s} \nu_i \mu_i^* + RT \sum_{i=1}^{s} \nu_i \ln a_i$$

$$= \Delta_r G^\ominus + RT \sum_{i=1}^{s} \ln a_i^{\nu_i}$$

Assuming μ_i^* goes to $\mu_i^\ominus$ std. state

$$\boxed{\Delta_r G = \Delta_r G^\ominus(T) + RT \ln \left(\Pi\, a_i^{\nu_i} \right)}$$

At Equilibrium, $\Delta_r G = 0$ so that

$$\ln K = -\frac{\Delta_r G^{\ominus}(T)}{RT}$$

where $K \equiv \prod a_i^{\nu_i}$

↳ Equilibrium Constant

** The value of an Equilibrium constant cannot be interpreted unless it is accompanied by a balanced chemical Equation and a specification of the standard state of each reactant and product **

Note that $\Delta_r G^{\ominus}(T)$ represents the reaction free energy for the hypothetical reaction of the unmixed reactants to form unmixed products at a temperature T and at the standard state pressure, $p^{\ominus}$.

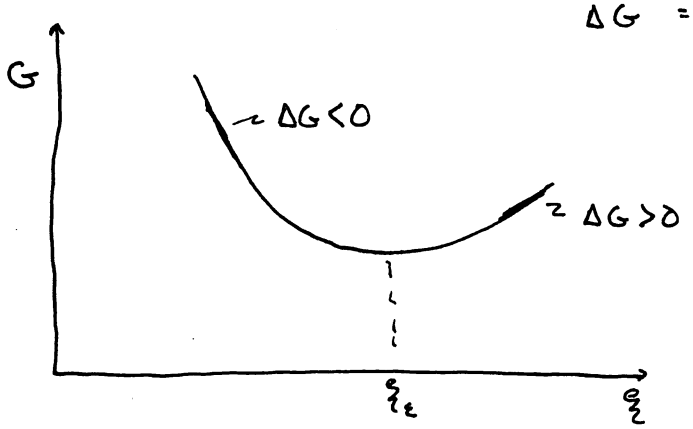
Also note that if any of the standard states are referenced to the pressure, p, instead of $p^{\ominus}$, then $\Delta_r G^{\ominus}$ will depend on both T & P.

Reaction Quotient

Equilibrium Condition

$$\sum_{i=1}^{s} \nu_i \mu_i = 0$$

$$\Delta G = 0$$



$$\Delta G(T,P,\underline{y}) \equiv \sum_{i=1}^{s} \nu_i \mu_i (T,P,\underline{y})$$

$\Delta G < 0$ reaction proceeds as written

$\Delta G > 0$ reaction proceeds in reverse direction

The most general form for the chemical potential is:

$$\mu_i (T,P,\underline{y}) = \mu_i^* (T,P) + RT \ln a_i$$

for gas species the standard state is typically $\mu_i^\ominus (T)$

and $$a_i (T,P,\underline{y}) = \frac{f_i (T,P,y)}{P^\ominus} = \frac{\gamma_i (T,P,y)\, P\, y_i}{P^\ominus}$$

for liquids or solids:

$$\mu_i^* (T,P) = \mu_i^\bullet (T,P)$$

$$a_i (T,P,x) = \gamma_i (T,P,x)\, x_i$$

} assume $\mu_i^\bullet (T,P^\ominus)$

or

$$\mu_i^* (T,P) = \mu_i^\ddagger (T,P)$$

$$a_i (T,P,x) = \gamma_i^\ddagger (T,P,x)^{\,m_i/m_\ominus}$$

Substituting $\mu_i(T,P,x)$ into ΔG:

$$\Delta G = \sum_{i=1}^{s} \nu_i \mu_i^*(T,P) + RT \sum_{i=1}^{s} \nu_i \ln a_i$$

$$= \sum_{i=1}^{s} \nu_i \mu_i^*(T,P) + RT \sum_{i=1}^{s} \ln a_i^{\nu_i}$$

$$\boxed{\Delta G = \Delta G^{\ominus}(T,P) + RT \ln \prod_{i=1}^{s} a_i^{\nu_i}}$$

or

$$\boxed{\Delta G = \Delta G^{\ominus}(T,P) + RT \ln Q(T,P,y)}$$

where $\Delta G^{\ominus}(T,P) \equiv \sum \nu_i \mu_i^*(T,P)$

reaction free energy for the hypothetical reaction of unmixed reactants to form unmixed products in their standard state at Temperature, T.

$Q(T,P,x) \equiv \prod a_i^{\nu_i}$ "Reaction Quotient"

$$= \frac{a_P^{\nu_P} a_B^{\nu_B} \cdots a_S^{\nu_S}}{a_1^{\nu_1} a_2^{\nu_2} \cdots a_{P-1}^{\nu_{P-1}}} \equiv \frac{[\text{Products}]^{\nu_i}}{[\text{reactants}]^{\nu_i}}$$

at Equilibrium $\Delta G = 0$ so that $\Delta G^{\ominus}(T,P) + RT \ln Q_{eq} = 0$

$$\boxed{Q_{eq} \equiv K = \exp\left\{ \frac{-\Delta G^{\ominus}(T,P)}{RT} \right\}}$$

↓ Equilibrium "Constant"

The value of the Equilibrium constant for a given reaction can not be interpreted unless it is accompanied by a balanced rxn and a clear specification of std. state of each reactant & product. Typically, the standard states will be at $P^{\ominus}$. Thus, the Equilibrium Constant, K, will only depend on T. If any of the standard states are instead referenced to a state at P, then $\Delta G^{\ominus}$ will depend on both T & P.

Note:

$$\Delta G = \Delta G^{\ominus} + RT \ln Q$$

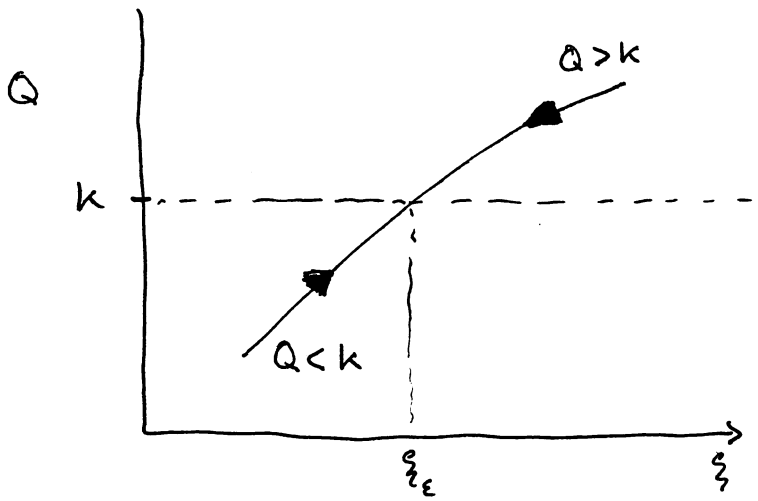
$$\Delta G^{\ominus} = -RT \ln K$$

$$\Delta G = -RT \ln K + RT \ln Q$$

$$\boxed{\Delta G = RT \ln Q/K}$$

if $Q < K$, $\Delta G < 0$ rxn proceeds in direction written

if $Q > K$, $\Delta G > 0$ rxn proceeds in reverse direction



Gas Phase Reactions

For gases, the standard state is the ideal gas state at T & $P^\ominus$. The activity of a gas species is given by,

$$a_i(T,P,y) = \frac{f_i(T,P,y)}{P^\ominus}$$

$$\Longrightarrow \boxed{K_f(T) = \prod_{i=1}^{s} \left(f_i/P^\ominus\right)^{\nu_i} \qquad \ln K_f = \frac{-\Delta_r G^\ominus(T)}{RT}}$$

K_f is only a function of T since the standard states only depend on T.

We can also relate K_f to the partial pressure, P_i, and y_i by noting

$$f_i(T,P,y) = P_i \gamma_i(T,P,y) = P\, y_i \gamma_i$$

$$\Longrightarrow \quad K_f(T) = K_p K_\gamma = \left(\frac{P}{P^\ominus}\right)^{\Delta\nu} K_y K_\gamma$$

where $K_p \equiv \prod_{i=1}^{s} \left(P_i/P^\ominus\right)^{\nu_i}$ & $K_y \equiv \prod_{i=1}^{s} y_i^{\nu_i}$

$K_\gamma \equiv \prod_{i=1}^{s} \gamma_i^{\nu_i}$ & $\Delta\nu \equiv \sum_{i=1}^{s} \nu_i$

Note that K_p, K_y & K_γ are general functions of T, P & y even though their product, K_f, is only a function of T!

Example: Dissociation Rxn of N_2O_4 (g)

Calculate the degree of dissociation of N_2O_4 (g) at constant T & P.

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

	N_2O_4 (g)	$2NO_2$ (g)	
initial amounts	N_0	0	
Equilibrium	$N_0 - \xi$	2ξ	(Total: $N_0 + \xi$)
mole fractions	$\frac{N_0 - \xi}{N_0 + \xi}$	$\frac{2\xi}{N_0 + \xi}$	

So, $K_p = \prod_{i=1}^{s} (P_i/p^\theta)^{\nu_i}$ assuming ideality

$$= (P/p^\theta)^1 K_y = (P/p^\theta) \frac{y^2_{NO_2}}{y_{N_2O_4}}$$

$$K_p = \left(\frac{P}{p^\theta}\right) \frac{N_0 + \xi}{N_0 - \xi} \left(\frac{2\xi}{N_0 + \xi}\right)^2 = \left(\frac{P}{p^\theta}\right) \frac{4\xi^2}{(N_0 - \xi)(N_0 + \xi)}$$

$$K_p = \left(\frac{P}{p^\theta}\right) \frac{4\xi^2}{N_0^2 - \xi^2}$$

Solving for ξ,

$$(N_0^2 - \xi^2) K_p = \left(\frac{P}{p^\theta}\right) 4\xi^2$$

$$\left(4\left(\frac{P}{p^\theta}\right) + K_p\right) \xi^2 = N_0^2 K_p$$

or $$\xi^2 = \frac{N_0^2 K_p}{4\left(\frac{P}{p^\theta}\right) + K_p}$$

it is convenient to introduce the dissociation fraction, α.

$$\alpha \equiv \frac{\xi}{N_0}$$

$$\Rightarrow \quad \alpha = \left[\frac{K_p}{4(p/p^\theta) + K_p} \right]^{1/2} = \frac{1}{\left[1 + 4/K_p (p/p^\theta) \right]^{1/2}}$$

For $T = 298K$,

$$\Delta_r G^\theta (298k) = 2 \Delta_f G^\theta_{NO_2} - \Delta_f G^\theta_{N_2O_4}$$

$$= [2(51.3) - 97.89] \quad (kJ)$$

$$= 4.73 \, kJ$$

$$\Rightarrow \ln K_f (298k) = \frac{-4.73 \times 10^3 \, J}{R \cdot 298k}$$

$$K_f = 0.148 \approx K_p \qquad \text{(assuming ideal gas, } k_\gamma = 1)$$

At $p = p^\theta$ $\quad \alpha = +0.189$

At $p = 3p^\theta$ $\quad \alpha = +0.110$

} only the positive solution is physically realizable.

Note that an increase in p reduces α.

Now Suppose this dissociation reaction were carried out in a constant volume container :

again, $$K_p = \left(\frac{p}{p^\theta}\right)^{\Delta\nu} K_y$$

For the N_2O_4 dissociation reaction $\Delta\nu = 1$ and we assume ideal gases :

$$\Rightarrow K_p = \left(\frac{NRT}{V p^\theta}\right) \frac{4\xi^2}{N_0^2 - \xi^2}$$

Substitute , $N = N_0 + \xi$

$$\Rightarrow K_p = \left(\frac{RT}{V p^\theta}\right) \frac{4\xi^2}{N_0 - \xi}$$

Solving for ξ :

$$4\xi^2 = (N_0 - \xi)\left(\frac{V p^\theta}{RT}\right) K_p$$

Substituting $\alpha = \xi/N_0$

$$4\alpha^2 = \left(\frac{V p^\theta}{N_0 RT}\right)(1-\alpha) K_p$$

Note that $N_0RT/V = P_0$ initial pressure, and $k_p \approx k_f(T)$ for an ideal gas.

$$\Rightarrow 4\alpha^2 = \left(\frac{p^\theta}{P_0}\right)(1-\alpha)\, k_f(T)$$

Thus, to solve the problem we need to know P_0 & $k_f(T)$.

Suppose $T = 298K$ & $P_0 = 3p^\theta$ & $k_f(298K) = 0.148$

Then, $$4\alpha^2 = (1-\alpha)\frac{.148}{3}$$

$$4\alpha^2 + 0.0493\alpha - 0.0493 = 0$$

$$\boxed{\alpha = +0.105}$$ physical answer

$$\alpha = -0.117$$ unphysical Answer

Determination of K_γ from K_p data

Consider the ammonia synthesis reaction at 450°C

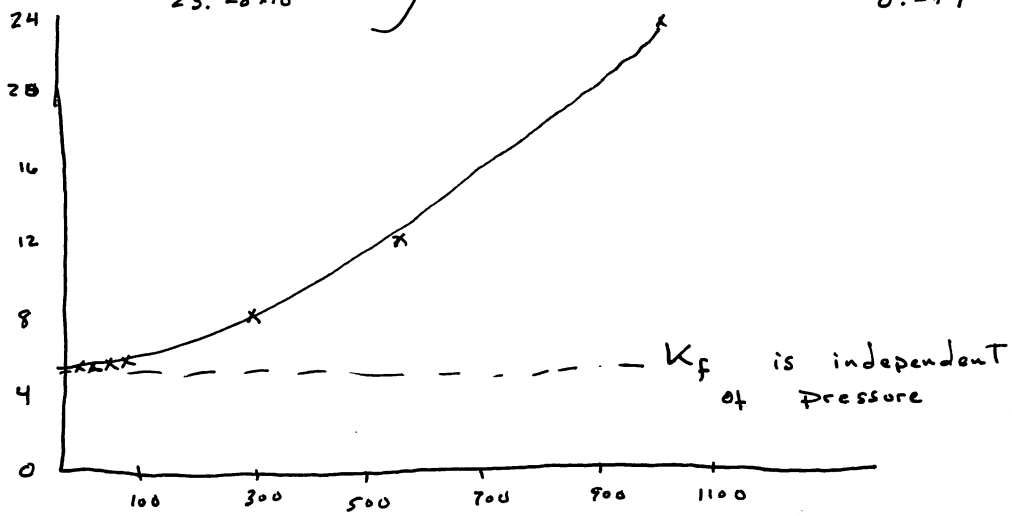
$$\frac{1}{2}\,N_2 + \frac{3}{2}\,H_2 \rightleftharpoons NH_3 \qquad \text{(requires catalyst)}$$

$$K_f = \frac{\left(f_{NH_3}/p^\theta\right)}{\left(f_{N_2}/p^\theta\right)^{1/2}\left(f_{H_2}/p^\theta\right)^{3/2}} = \frac{\left(P_{NH_3}/p^\theta\right)}{\left(P_{N_2}/p^\theta\right)^{1/2}\left(P_{H_2}/p^\theta\right)^{3/2}} \qquad K_\gamma = K_p K_\gamma$$

$K_p(P)$ can be determined by spectroscopic or chemical measurements. The data at 450°C is shown below.

P_{Total} (bar)	K_p	$K_\gamma = K_f/K_p$
10	6.59×10^{-3}	0.986
30	6.76×10^{-3}	0.962
50	6.90×10^{-3}	0.942
100	7.25×10^{-3}	0.897
300	8.84×10^{-3}	0.735
600	12.94×10^{-3}	0.502
1000	23.28×10^{-3}	0.279

from this data we can extract K_f, K_γ & ΔG^θ (see graph)



$$K_f = \lim_{P\to 0} K_p$$

Example: Effects of Initial Composition on Reaction Equilibria

Consider the equilibrium for the production of methanol from CO & H_2 gas.

$$CO\ (g) + 2\,H_2\ (g) \rightleftharpoons CH_3OH\ (g)$$

(A) First we'll consider an <u>Equimolar</u> mixture of CO (g) and H_2 (g) at 500 K and $P = 1$ bar, given that $K_f(500\,K) = 6.23 \times 10^{-3}$.

	CO	H_2	CH_3OH
Initial moles:	n_0	n_0	0
Equilibrium:	$n_0 - \xi$	$n_0 - 2\xi$	ξ

$$\Rightarrow n_{Total} = 2n_0 - 2\xi = 2(n_0 - \xi)$$

	CO	H_2	CH_3OH
Equil. y_i:	$\frac{1}{2}$	$\frac{n_0 - 2\xi}{2(n_0 - \xi)}$	$\frac{\xi}{2(n_0 - \xi)}$

So, $$K_y = \frac{\xi}{2(n_0 - \xi)} \left(\frac{2^2 (n_0 - \xi)^2}{(n_0 - 2\xi)^2} \right) \left(\frac{2}{1} \right)$$

$$K_y = \frac{4\xi (n_0 - \xi)}{(n_0 - 2\xi)^2}$$

Define $\alpha \equiv \xi / n_0$ "fractional extent of reaction"

$$\boxed{K_y = \frac{4\alpha(1-\alpha)}{(1-2\alpha)^2}}$$

Recall, $K_f(T) = \left(\frac{P}{P^\ominus}\right)^{\Delta\nu} K_y K_\gamma$

For this problem, $P = P^\ominus$ & we will assume $K_\gamma = 1$

$$K_y \sim K_f(T) = 6.25 \times 10^{-3} \quad @ \quad 500K$$

$$\frac{4\alpha(1-\alpha)}{(1-2\alpha)^2} = 6.25 \times 10^{-3}$$

Solving this quadratic equation for α we obtain.

$$\boxed{\alpha = 0.00155}$$

or $y_{CO} = 1/2$

$$y_{H_2} = \frac{1-2\alpha}{2(1-\alpha)} = 0.4992$$

$$y_{CH_3OH} = \frac{\alpha}{2(1-\alpha)} = 0.0008$$

(B) Now we'll consider the same reaction at 100 bar and a 2:1 mixture of H_2 / CO gas.

	CO	H_2	CH_3OH	
Initial moles	n_0	$2n_0$	0	
Equilibrium	$n_0 - \xi$	$2n_0 - 2\xi$	ξ	$\Rightarrow n_{total} = 3n_0 - 2\xi$
Mole fraction	$\frac{n_0 - \xi}{3n_0 - 2\xi}$	$\frac{2n_0 - 2\xi}{3n_0 - 2\xi}$	$\frac{\xi}{3n_0 - 2\xi}$	
or	$\frac{1-\alpha}{3-2\alpha}$	$\frac{2(1-\alpha)}{3-2\alpha}$	$\frac{\alpha}{3-2\alpha}$	$\boxed{\alpha \equiv \frac{\xi}{n_0}}$

$$\Rightarrow K_y = \frac{\alpha}{3-2\alpha} \cdot \frac{(3-2\alpha)^2}{2^2(1-\alpha)^2} \frac{(3-2\alpha)}{(1-\alpha)} = \frac{\alpha(3-2\alpha)^2}{4(1-\alpha)^3}$$

$$K_f = \left(\frac{P}{P^\theta}\right)^{\Delta\nu} K_y K_\gamma = 6.25 \times 10^{-3}$$

if $P = 100$ bar $\Rightarrow K_\gamma \cong 1$ $\Rightarrow \Delta\nu = -2$,

$$\Rightarrow \frac{1}{100^2} \frac{\alpha(3-2\alpha)^2}{4(1-\alpha)^3} = 6.25 \times 10^{-3}$$

$$\alpha(9 - 12\alpha + 4\alpha^2) = 6.25 \times 10^{-3} \times 10^4 \; 4(1-\alpha)(1-2\alpha+\alpha^2)$$

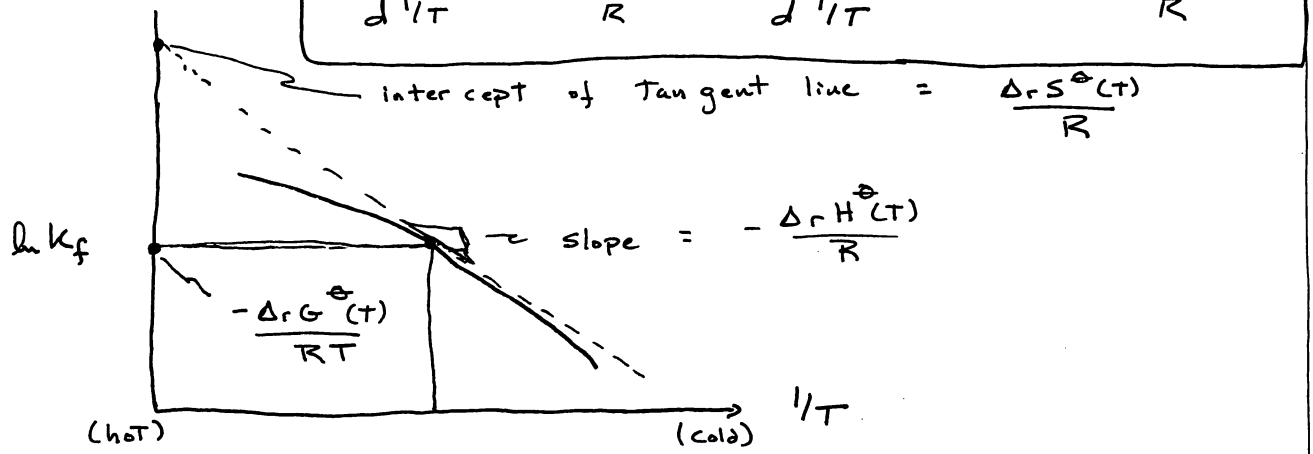
This cubic Eqn. can be solved by Successive Iteration or by Mathematica.

$$\boxed{\alpha = 0.817}$$

Temperature Dependence of k_f

Recall, $\ln k_f(T) = -\frac{\Delta_r G^\ominus(T)}{RT} = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}$

$$\frac{\partial \ln k_f}{d\,1/T} = -\frac{1}{R}\,\frac{d\,\Delta_r G^\ominus/T}{d\,1/T} = -\frac{\Delta_r H^\ominus(T)}{R}$$



Endothermic Rxn $\Delta_r H^\ominus > 0$ k_f increases with T

Exothermic Rxn $\Delta_r H^\ominus < 0$ k_f decreases with T

Integrating the Temperature dependence of $\ln k_f$:

$$\ln k_f(T) = \ln k_f(T_o) - \int_{1/T_o}^{1/T} \frac{\Delta_r H^\ominus(T')}{R}\, d\,1/T$$

Approximation: $-\Delta_r H^\ominus$ is independent of T ($\Delta_r C_p^\ominus = 0$)

$$\Rightarrow \boxed{\ln k_f(T) = \ln k_f(T_o) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)}$$

More Exact: $\Delta_r C_p^\ominus(T)$ is known:

$C_{p,i}^\ominus(T)$ data is typically given as a polynomial Expansion in T,

$$C_{p,i}^\ominus(T) = a_i + b_i T + c_i T^2 + \cdots$$

So, stopping at second order,

$$C_{p,i}^{\ominus}(T) = a_i + b_i T + c_i T^2$$

$$\Rightarrow \quad \Delta_r C_p^{\ominus}(T) = \sum_{i=1}^{c} \nu_i \left(a_i + b_i T + c_i T^2 \right)$$

$$= A + BT + CT^2$$

where, $A \equiv \sum_{i=1}^{s} \nu_i a_i \qquad B \equiv \sum_{i=1}^{s} \nu_i b_i \qquad C \equiv \sum_{i=1}^{s} \nu_i c_i$

$$\Longrightarrow \quad d\Delta_r H^{\ominus} = \left[A + BT + CT^2 \right] dT$$

or

$$\Delta_r H^{\ominus}(T) = \Delta H_0 + AT + \frac{BT^2}{2} + \frac{CT^3}{3}$$

In this eqn. ΔH_0 is an integration constant (the value of ΔH at 0 K) & can be evaluated from the above eqn. if $\Delta_r H^{\ominus}$ is known at some temperature (Typically 298 K) (Note: $\Delta H_0 \neq \Delta_r H^{\ominus}(298\,K)$)

Finally we can obtain $\ln k_f(T)$:

Recall, $$d \ln k_f = \frac{-\Delta_r H^{\ominus}(T)}{R} d\frac{1}{T} = \frac{\Delta_r H^{\ominus}}{RT^2} dT$$

$$\int d \ln k_f = \int \left(\frac{\Delta H_0}{RT'^2} + \frac{A}{RT'} + \frac{B}{2R} + \frac{CT'}{3R} \right) dT'$$

$$\Longrightarrow \quad \ln k_f(T) = I - \frac{\Delta H_0}{RT} + \frac{A}{R} \ln T + \frac{BT}{2R} + \frac{CT^2}{6R}$$

where I is another integration constant which can be evaluated if k_f is known at some temperature (Typically 298 K).

Example: Temperature dependence of N_2O_4 dissociation

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$\Delta_f G^\ominus (298\,K)$	$97.89\ kJ$	$2(51.3)\ kJ$	$\rightarrow \Delta_r G^\ominus (298) = 4.73\ kJ$
$\Delta_f H^\ominus (298K)$	$9.2\ kJ$	$2(33.1)\ kJ$	$\rightarrow \Delta_r H^\ominus (298) = 57.0\ kJ$
$\Delta_r C_p^\ominus (298K)$	$77.3\ kJ$	$2(36.9)\ kJ$	$\rightarrow \Delta_r C_p^\ominus (298) = -3.5\ J/K$

if we assume $\Delta_r C_p^\ominus$ is constant then:

$$A \equiv \Delta_r C_p^\ominus = -3.5\ J/K$$

$$B \equiv 0$$

$$C \equiv 0$$

$$\vdots$$

$\Delta_r H^\ominus (T) = \Delta H_0 + AT$, so we can solve for ΔH_0

$57 \times 10^3\ J = \Delta H_0 + (-3.5\ J/K)(298\ K)$

$\Rightarrow \boxed{\Delta H_0 = 58043\ J}$

$$\boxed{\ln k_f (298) = \frac{-\Delta G^\ominus (298\,K)}{298\,K\ R} = -1.91}$$

Recall from p. 217, $\dfrac{d \ln k_f}{d\,1/T} = -\dfrac{1}{R} \Delta_r H^\ominus (T)$

This leads to $\ln k_f (T) = I - \dfrac{\Delta H_0}{R} + \dfrac{A}{R} \ln T$ (p. 225)

for B & C equal to zero

Since $\ln k_f (298K)$ is known, we can solve for I,

$$I = 4.28$$

Now we have our general Equation for $\ln k_f(T)$

$$\ln k_f(T) = I - \frac{\Delta H_0}{RT} + \frac{A}{R}\ln T + \frac{BT}{2R} + \frac{CT^2}{6R}$$

$$\ln k_f(T) = 4.28 - \frac{58 \times 10^3}{RT} + \frac{-3.5}{R}\ln T$$

for $T = 373k$ $\quad \ln k_f = 1.77$

$$k_f = 5.89$$

Recall our general Eqn. for $\alpha(T)$ for the dissociation of N_2O_4 :

$$\alpha(T) = \frac{1}{\left[1 + \frac{4}{K_p}\left(P/P^0\right)\right]^{1/2}}$$

Now we assume $K_p \sim K_f$ (ideal gas)

for $P = P^0$ and $T = 373k$ we have

$$\boxed{\alpha(373k) = 0.77}$$

Compared to 0.189 @ 298 k.

Heterogeneous Equilibria

In the following we will consider chemical reactions involving several phases. In particular, gaseous species and a pure solid or liquid phase. One example is the decarboxylization of $CaCO_3$ (s):

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

where $CaCO_3$ (s) and CaO (s) are <u>pure immiscible</u> solid phases.

Again, the condition of chemical equilibrium is that:

$$\boxed{\sum_{i=1}^{S} \nu_i \mu_i = 0 \qquad \text{Chemical Equilibrium}}$$

where the μ_i are the chemical potentials of the components involved in the rxn and the ν_i are the stoichiometric coefficients.

Recall, we can in general write the μ_i for a chemical component in any phase as:

$$\mu_i(T,P,\underline{x}) = \mu_i^*(T,P) + RT \ln a_i(T,P,\underline{x})$$

For gaseous species we use the ideal gas state at $P^\ominus$ as the standard state and the activity is given by the fugacity ratio: $f_i(T,P,y)/P^\ominus$

gaseous species

$$\boxed{\mu_i^{(g)}(T,P,\underline{y}) = \mu_i^\ominus(T) + RT \ln \frac{f_i(T,P,\underline{y})}{P^\ominus}}$$

$$\boxed{a_i(T,P,\underline{y}) \equiv \frac{f_i(T,P,y)}{P^\ominus}}$$

For solid and liquid species we can also use an ideal gas reference state. However, it is often more convenient to use the <u>pure solid</u> or <u>pure liquid</u> at T & P as the reference state.

$$\underbrace{\mu_i^{(s)}(T,P,\underline{x})}_{\text{impure solid component @ } T,P,\underline{x}} = \underbrace{\mu_i^{\bullet(s)}(T,P)}_{\text{pure solid component @ } T,P} + RT \ln a_i(T,P,\underline{x})$$

Therefore, whenever we are dealing with pure solid or liquid phases the activities are equal to unity.

$$a_i = 1 \qquad \text{pure solids and liquids when referenced to } \mu_i^{\bullet}(T,P)$$

It is important to remember that <u>with this choice</u> the standard state chemical potentials of liquid and solid phases are pressure dependent.

Going back to our original equation for chemical equilibrium we have:

$$\sum_{i=1}^{s} \nu_i \mu_i = 0 \qquad \text{at equilibrium}$$

Assuming the condensed phases are pure:

$$\underbrace{\sum_{i=1}^{n} \nu_i \left(\mu_i^{\theta}(T) + RT \ln f_i/P^{\theta}\right)}_{\text{gaseous species}} + \underbrace{\sum_{i=n+1}^{s} \nu_i \mu_i^{\bullet}(T,P)}_{\text{condensed species}} = 0$$

$$RT \ln K_f' = -\sum_{i=1}^{n} \nu_i \mu_i^{\ominus}(T) - \sum_{i=n+1}^{s} \nu_i \mu_i^{\bullet}(T,P)$$

where $K_f' \equiv \prod_{i=1}^{n} \left(f_i/p^{\ominus}\right)^{\nu_i}$ "partial Equilibrium constant"

The first term on the right hand side of the top Equilibrium refers to the standard state chemical potentials of the gaseous species at T & $P^{\ominus}$.

The 2nd Term refers to the chemical potentials of the pure reference solid and/or liquid components at T and P.

Note that K_f' is a function of both T & P. However, the P dependence is typically fairly weak since the pressures involved in rxns with gas phases are typically very small.

Recall that the pressure dependence of $\mu_i^{\bullet}(T,P)$ is given by,

$$\left(\frac{\partial \mu_i^{\bullet}}{\partial P}\right)_T = v_i^{\bullet}(T,P) \quad \text{molar volume of pure } i$$

$$\Longrightarrow \mu_i^{\bullet}(T,P) = \mu_i^{\bullet}(T,P^{\ominus}) + \int_{P^{\ominus}}^{P} v_i^{\bullet}(T,P)\, dP$$

For solids and liquids the pressure correction is generally quite small since v_i^* is small.

Therefore, when we are dealing with heterogeneous chemical reactions involving a gaseous phase, the pressure are small and we can write,

$$\mu_i^*(T,P) \approx \mu_i^*(T,P^\ominus)$$

$$\Longrightarrow \quad RT \ln K_f' \approx \underbrace{-\sum_{i=1}^{n} \nu_i \mu_i^\ominus(T)}_{\text{gaseous species}} \underbrace{- \sum_{i=n+1}^{s} \nu_i \mu_i^*(T)}_{\text{Solid \& liquid Species}}$$

or

$$\boxed{\ln K_f' \cong -\frac{\Delta_r G^\ominus(T)}{RT}}$$

Example: Decarboxylization of $CaCO_3(s)$

Given that $CaCO_3(s)$ is contained in a closed vessel at a pressure P, at what temperature will $CO_2(g)$ be evolved.

$$RT \ln K_f' = RT \ln \frac{f_{CO_2}}{P^\theta} \cong -\Delta_r G^\theta(T)$$

{ neglecting the P-dependence of $\mu^{(s)}$.

where, $\Delta_r G^\theta(T) = \mu^\theta_{CO_2(g)}(T) + \mu^\bullet_{CaO(s)}(T, P^\theta) - \mu^\bullet_{CaCO_3(s)}(T, P)$

$$\ln \frac{P_{CO_2}}{P^\theta} \approx \frac{-\Delta_r G^\theta(T)}{RT}$$

or

$$\log \frac{P_{CO_2}}{P^\theta} \approx \frac{-\Delta_r G^\theta(T)}{2.303\,RT}$$

Thus, to find P_{CO_2} at any T we need to know $\Delta_r G^\theta$ as a function of T.

To a first approximation lets consider that $\Delta_r C_p^\theta \approx 0$. With this approximation:

$\Delta_r H^\theta$, $\Delta_r S^\theta$ } are both independent of Temperature if $\Delta_r C_p^\theta = 0$

Therefore, Since $\Delta G = \Delta H - T\Delta S$, we can write

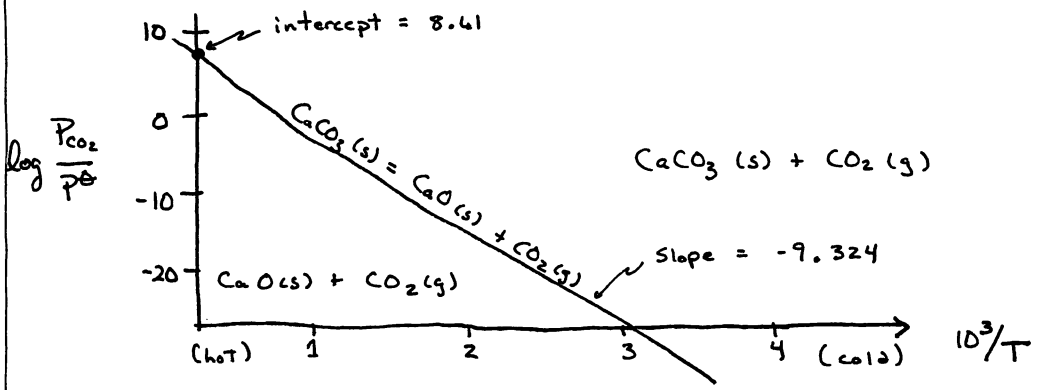
$$\Delta_r G^\theta(T) \cong \Delta_r H^\theta(298k) - T\Delta S^\theta(298k)$$

For the decarboxylization reaction we have:

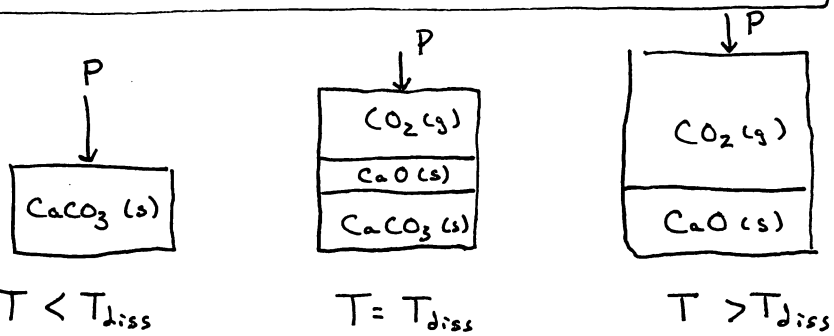
$$\frac{\Delta_r S^\ominus(298\,K)}{2.303\ R} = \frac{\overset{(O_2(g))}{213.74\ J/K.mol} + \overset{(CaO(s))}{39.75\ J/K.mol} - \overset{(CaCO_3(s))}{88.7\ J/K.mol}}{2.303\ R} = 8.61$$

$$\frac{\Delta_r H^\ominus(298K)}{2.303\ RT} = \frac{(-393.51 - 635.09 - 1207.13)*10^3}{2.303\ RT} = \frac{9324}{T}$$

$$\Rightarrow \boxed{\log \frac{P_{CO_2}}{P^\ominus} = 8.61 - \frac{9324}{T}} = \frac{-\Delta_r G^\ominus(T)}{2.303\ RT}$$



For $P_{CO_2} = 1$ bar $\Rightarrow T_{dissociation} = 1083$ K



$T < T_{diss}$ $\quad T = T_{diss}$ $\quad T > T_{diss}$

In air $P_{CO_2} = 0.2$ bar $\Rightarrow T_{diss} = 1002$ K

Example : Buffer Reactions.

The oxygen fugacity in a synthetic reaction can be accurately controlled and manipulated if we can establish a side reaction of pure compounds involving oxygen. Suppose, for example, that we have a closed reaction vessel where $Zn(s)$ and $ZnO(s)$ coexist together in Equilibrium at some T and P. The oxygen fugacity is established by the reaction:

$$\underset{\text{pure oxide phase}}{ZnO(s)} \rightleftharpoons \underset{\text{pure metal phase}}{Zn(s)} + \tfrac{1}{2} O_2(g)$$

$$RT \ln k_f' \equiv RT \ln \left(\frac{f_{O_2}}{P^\theta}\right)^{1/2} = -\left[\frac{1}{2}\mu_{O_2}^\theta(T) + \mu_{Zn(s)}^\bullet(T,P) - \mu_{ZnO(s)}^\bullet(T,P)\right]$$

$$= -\left[\frac{1}{2}\mu_{O_2}^\theta(T) + \mu_{Zn(s)}^\bullet(T,P^\theta) - \mu_{ZnO(s)}^\bullet(T,P^\theta)\right] - \int_{P^\theta}^{P} (v_{Zn(s)}^\bullet - v_{ZnO(s)}^\bullet)\,dP$$

$$\Rightarrow \boxed{\log\left(\frac{f_{O_2}}{P^\theta}\right) \cong \frac{-2\,\Delta_r G^\theta(T)}{2.303\,RT} - \frac{(v_{Zn(s)}^\bullet - v_{ZnO(s)}^\bullet)(P-P^\theta)}{2.303\,RT}}$$

assuming the solids are incompressible

Again, lets assume that $\Delta_r C_p^\theta \simeq 0$ so we can write,

$$\frac{\Delta_r G^\theta(T)}{2.303\,RT} \cong \frac{\Delta_r H^\theta(298K)}{2.303\,RT} - \frac{\Delta_r S^\theta(298K)}{2.303\,R}$$

$$\frac{\Delta_r H^\theta(298K)}{2.303\,RT} = \frac{\left(0 + \tfrac{1}{2}\,0 - (+348.28 \times 10^3)\right)}{2.303\,RT} = \frac{18.18 \times 10^3}{T}$$

$$\frac{\Delta_r S^\theta(298K)}{2.303\,R} = \left(\frac{41.63 + \tfrac{1}{2}(205.15) - 43.64}{2.303\,R}\right) = 5.25$$

$$\Rightarrow \log \frac{f_{O_2}}{P^\theta} = 10.5 - \frac{36.36 \times 10^3}{T}$$