Thermodynamics of Materials

13th Lecture

2008. 4. 23 (Wednesday)

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partial molar quantity

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

partial molar Gibbs free energy

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

partial molar operator $\left(\frac{\partial}{\partial n_i}\right)_{P,T,n_j}$

$$\mu_k \equiv \left(\frac{\partial U'}{\partial n_k}\right)_{S',V',n_{j\neq k}} \neq \bar{U}_k = \left(\frac{\partial U'}{\partial n_k}\right)_{T,P,n_{j\neq k}}$$

$$\mu_k \equiv \left(\frac{\partial H'}{\partial n_k}\right)_{S',P,n_{j\neq k}} \neq \bar{H}_k = \left(\frac{\partial H'}{\partial n_k}\right)_{T,P,n_{j\neq k}}$$

$$\mu_k \equiv \left(\frac{\partial F'}{\partial n_k}\right)_{T,V',n_{j\neq k}} \neq \bar{F}_k = \left(\frac{\partial F'}{\partial n_k}\right)_{T,P,n_{j\neq k}}$$

$$\mu_k \equiv \left(\frac{\partial G'}{\partial n_k}\right)_{T,P,n_{j\neq k}} = \bar{G}_k = \left(\frac{\partial G'}{\partial n_k}\right)_{T,P,n_{j\neq k}}$$

$$G' = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots} n_i + \left(\frac{\partial G'}{\partial n_j}\right)_{T,P,n_i,n_k,\ldots} n_j + \left(\frac{\partial G'}{\partial n_k}\right)_{T,P,n_i,n_j,\ldots} n_k + \ldots$$

$$G' = \bar{G}_i n_i + \bar{G}_j n_j + \bar{G}_k n_k + \ldots = \sum \bar{G}_n n_n$$

$$G' = G'\left(T,P,n_i,n_j,n_k,\ldots\right)$$

$$dG' = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots} dn_i + \left(\frac{\partial G'}{\partial n_j}\right)_{T,P,n_i,n_k,\ldots} dn_j + \left(\frac{\partial G'}{\partial n_k}\right)_{T,P,n_i,n_j,\ldots} dn_k + \ldots$$

$$dG' = \bar{G}_i dn_i + \bar{G}_j dn_j + \bar{G}_k dn_k + \ldots$$

For pure substances, chemical potential becomes molar Gibbs free energy at constant P and T.

For mixtures, chemical potential becomes partial molar Gibbs free energy.

The partial molar Gibbs free energy is known as a function of T, P and composition.
Determine the partial molar quantities of
$\bar{S}$, $\bar{V}$, $\bar{H}$, $\bar{U}$ and $\bar{F}$.

$$\bar{S}_k = -\left(\frac{\partial \bar{G}_k}{\partial T}\right)_{P,n_k} = -\left(\frac{\partial \mu_k}{\partial T}\right)_{P,n_k} \qquad \bar{V}_k = \left(\frac{\partial \bar{G}_k}{\partial P}\right)_{T,n_k} = \left(\frac{\partial \mu_k}{\partial P}\right)_{T,n_k}$$

$$\bar{H}_k = \bar{G}_k + T\bar{S}_k = \mu_k - T\left(\frac{\partial \mu_k}{\partial T}\right)_{P,n_k}$$

$$\bar{U}_k = \bar{H}_k - P\bar{V}_k = \mu_k - T\left(\frac{\partial \mu_k}{\partial T}\right)_{P,n_k} - P\left(\frac{\partial \mu_k}{\partial P}\right)_{T,n_k}$$

$$\bar{F}_k = \bar{U}_k - T\bar{S}_k = \mu_k - P\left(\frac{\partial \mu_k}{\partial P}\right)_{T,n_k}$$

Consider the binary solution of components A and B. We have information about the molar Gibbs free energy of the mixture as a function of composition.

How can we determine the partial molar Gibbs energy of A?

$$\bar{G}_A = G_m + X_B \frac{dG_m}{dX_A}$$

$$\bar{G}_A = G_m + \left(1 - X_A\right) \frac{dG_m}{dX_A}$$

For a binary alloy, the molar free energy of the mixture becomes

$$G' = \bar{G}_A n_A + \bar{G}_B n_B \qquad dG' = \bar{G}_A dn_A + \bar{G}_B dn_B$$

$$G_m = \bar{G}_A X_A + \bar{G}_B X_B$$

$$dG_m = \bar{G}_A dX_A + \bar{G}_B dX_B$$

$$\frac{dG_m}{dX_A} = \bar{G}_A - \bar{G}_B$$

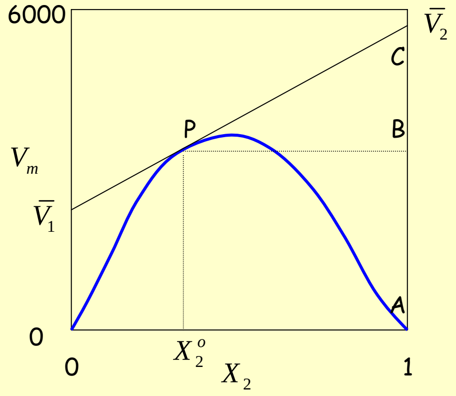
$$X_B \frac{dG_m}{dX_A} = X_B\bar{G}_A - X_B\bar{G}_B$$

$$G_m + X_B\frac{dG_m}{dX_A} = \bar{G}_A\left(X_A + X_B\right) = \bar{G}_A$$

$$\bar{G}_A = G_m + X_B\frac{dG_m}{dX_A}$$

$$\bar{G}_B = G_m + X_A\frac{dG_m}{dX_B}$$

Graphical Determination of Partial Molal Properties



$$V_m = X_1\bar{V}_1 + X_2\bar{V}_2$$

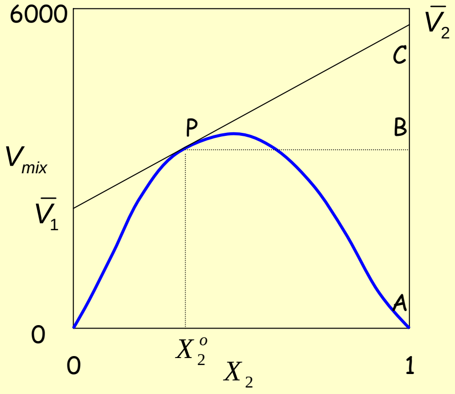
$$\bar{V}_2 - \bar{V}_1 = ?$$

$$\bar{V}_2 - \bar{V}_1 = \frac{dV_m}{dX_2}$$

$$\bar{V}_2 = ?$$

$$\bar{V}_2 = V_m + \left(1 - X_2\right)\frac{dV_m}{dX_2}$$

Graphical Determination of Partial Molal Properties



$$\frac{dV_{mix}}{dX_2} = \frac{BC}{PB}$$

$$(1 - X_2) = PB$$

$$V_{mix} = AB$$

$$\bar{V}_2 = V_{mix} + (1 - X_2)\frac{dV_{mix}}{dX_2} = AB + PB \cdot \frac{BC}{PB} = AB + BC = AC$$

Consider the binary solution of components A and B. We have information about the partial molar Gibbs free energy of B as a function of composition.

How can we determine the partial molar Gibbs energy of A? Derive the expression.

$$X_A dG_A + X_B dG_B = 0$$

Derive the Gibbs-Duhem equation.

$$V' = \sum_{k=1}^{c} \overline{V}_k n_k \qquad dV'_{T,P} = \sum_{k=1}^{c} \overline{V}_k dn_k$$

$$dV' = \sum_{k=1}^{c} d\left(\overline{V}_k n_k\right) = \sum_{k=1}^{c} \left[\overline{V}_k dn_k + n_k d\overline{V}_k\right] = \sum_{k=1}^{c} \overline{V}_k dn_k$$

$$\sum_{k=1}^{c} n_k d\overline{V}_k = 0$$

Gibbs-Duhem Equation;
→ holds for all partial molar quantities

$$dB'_{T,P} = \sum_{k=1}^{c} \overline{B}_k dn_k \qquad B' = \sum_{k=1}^{c} \overline{B}_k n_k$$

$$\sum_{k=1}^{c} n_k d\overline{B}_k = 0 \rightarrow n_1 d\overline{B}_1 + n_2 d\overline{B}_2 = 0$$

$$n_1 d\overline{G}_1 + n_2 d\overline{G}_2 = 0$$

$$n_A d\mu_A + n_B d\mu_B = 0$$

Evaluation of Partial Molar Properties

Partial molar properties can be evaluated from experimental data of two broad types:

(1) Measurements of the corresponding total properties of the solution as a function of composition.

$$\bar{G}_A = G_m + X_B \frac{dG_m}{dX_A}$$

(2) Measurements of the partial molar property for one of the components as a function of composition.

$$n_A d\mu_A + n_B d\mu_B = 0$$

Consider the binary solution of components A and B. We have information about the activity of B as a function of composition.

Derive the expression to determine the activity of A.

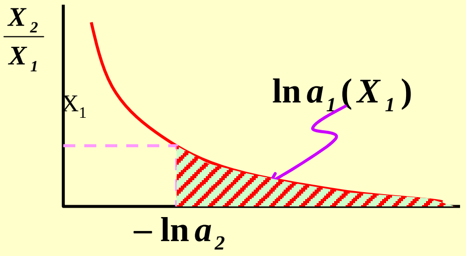
$$X_1 d\mu_1 + X_2 d\mu_2 = 0$$

$$X_1 d\ln a_1 + X_2 d\ln a_2 = 0$$

$$\int_{X_1=1}^{X_i} d\ln a_1 = -\int_{X_1=1}^{X_i} \frac{X_2}{X_1}\, d\ln a_2$$

$$\ln a_1(X_1) - \cancelto{0}{\ln a_1(X_1 = 1)} = -\int_{X_i=1}^{X_i} \frac{X_2}{X_1}\, d\ln a_2$$

$$\ln a_1(X_1) = -\int_{X_i=1}^{X_i} \frac{X_2}{X_1}\, d\ln a_2$$



i) As $X_2 \rightarrow 1$, $X_2/X_1 \rightarrow \infty$

ii) As $X_2 \rightarrow 0$, $a_2 \rightarrow 0$ and $\ln a_2 \rightarrow -\infty$.
i.e. tails to ∞.

How can you avoid the difficulty that $-\ln a_2$ goes to infinity as $X_1 \rightarrow 1$?

Use activity coefficient instead of activity.

To avoid the difficulty that
$-\ln a_2$ goes to infinity as $X_1 \rightarrow 1$,

$$X_1 d\mu_1 + X_2 d\mu_2 = 0$$

$$X_1 d\ln a_1 + X_2 d\ln a_2 = 0$$

$$(X_1 d\ln X_1 + X_2 d\ln X_2) + (X_1 d\ln \gamma_1 + X_2 d\ln \gamma_2) = 0$$

$$X_1 + X_2 = 1 \qquad dX_1 + dX_2 = 0$$

$$X_1 \frac{dX_1}{X_1} + X_2 \frac{dX_2}{X_2} = 0 \quad \rightarrow X_1 d\ln X_1 + X_2 d\ln X_2 = 0$$

$$\cancelto{0}{(X_1 d\ln X_1 + X_2 d\ln X_2)} + (X_1 d\ln \gamma_1 + X_2 d\ln \gamma_2) = 0$$

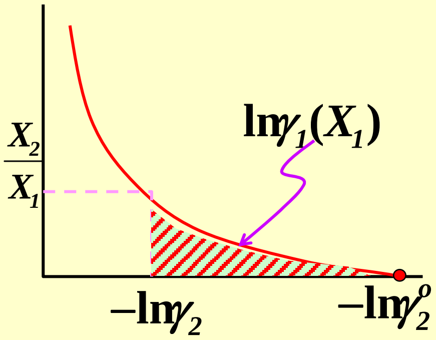
$$\Leftarrow X_1 d\ln X_1 + X_2 d\ln X_2 = 0$$

$$d\ln a_1 = -\frac{X_2}{X_1} d\ln a_2$$

$$d\ln \gamma_1 = -\frac{X_2}{X_1} d\ln \gamma_2$$

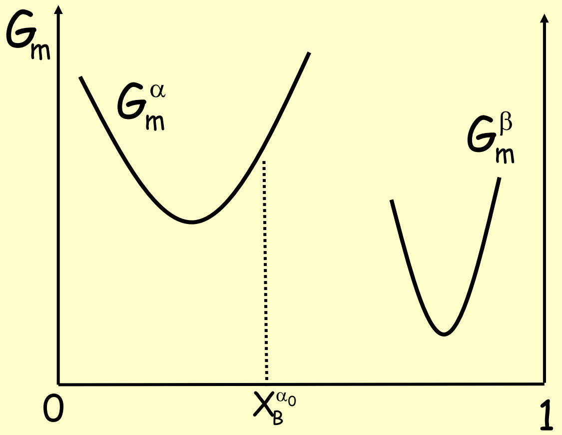
$$\int_{X_i=1}^{X_i} d\ln\gamma_1 = -\int_{X_i=1}^{X_i} \frac{X_2}{X_1} d\ln\gamma_2$$

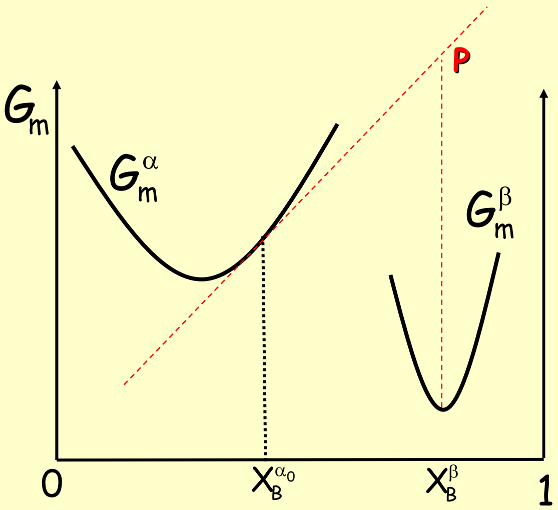
$$\ln\gamma_1(X_1) = -\int_{X_i=1}^{X_i} \frac{X_2}{X_1} d\ln\gamma_2$$



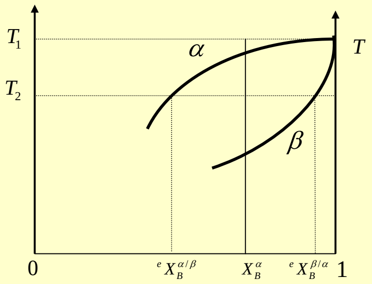
$$\Leftarrow \begin{cases} \lim\limits_{X_1\to 1} \ln\gamma_2 \longrightarrow \ln\gamma_2^o \\ \lim\limits_{\ln\gamma_2\to 0} \frac{X_2}{X_1} \longrightarrow +\infty \end{cases}$$

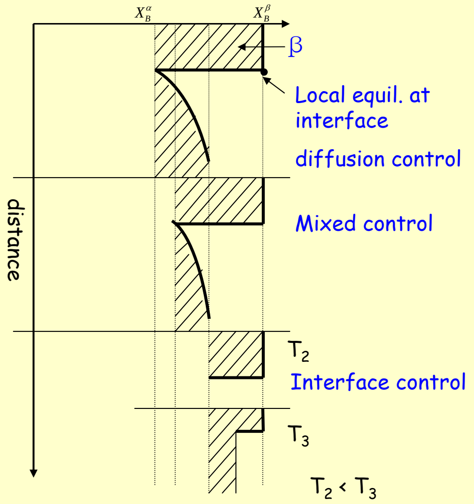
What is the driving force for precipitation of β from α?

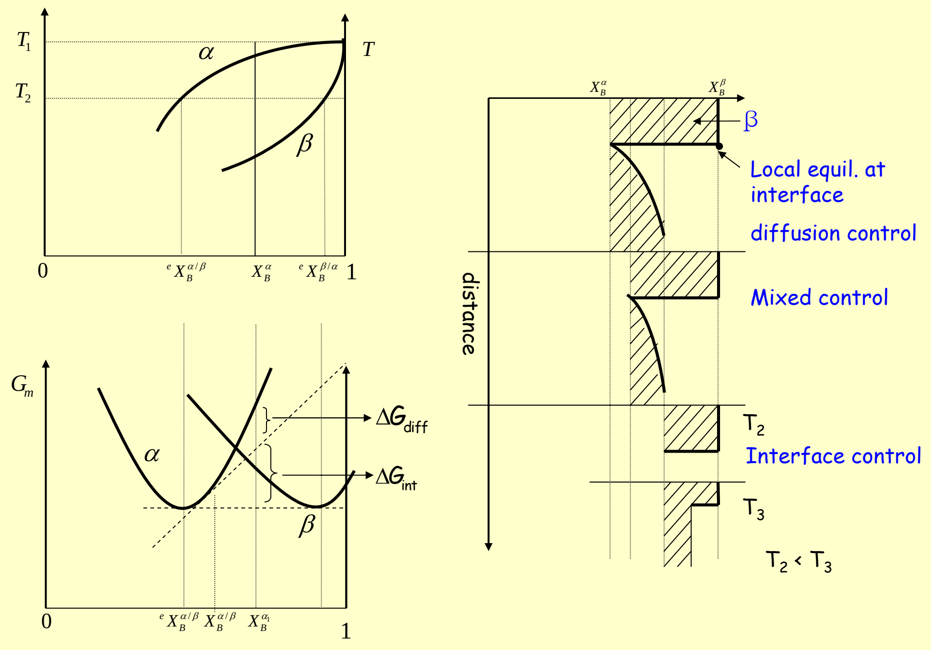




$$\Delta G = \bar{G}_A X_A^\beta + \bar{G}_B X_B^\beta - G_m^\beta(X_B^\beta)$$







Local equil. at interface

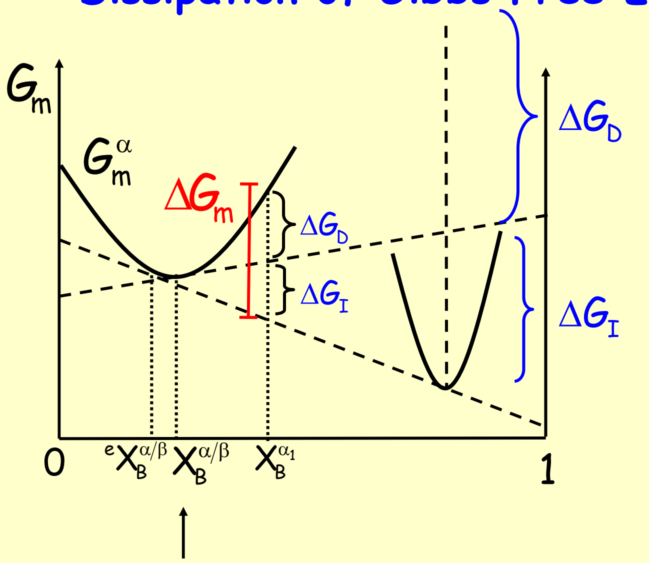
diffusion control

Mixed control

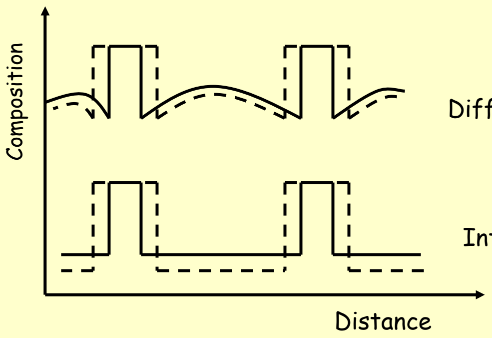
Interface control

$T_2 < T_3$

Dissipation of Gibbs Free Energy



Composition of α at the β interface



$J_D = J_I$ → mass conservation in serial kinetic path

$J_D \approx M_D \cdot \Delta G_D$

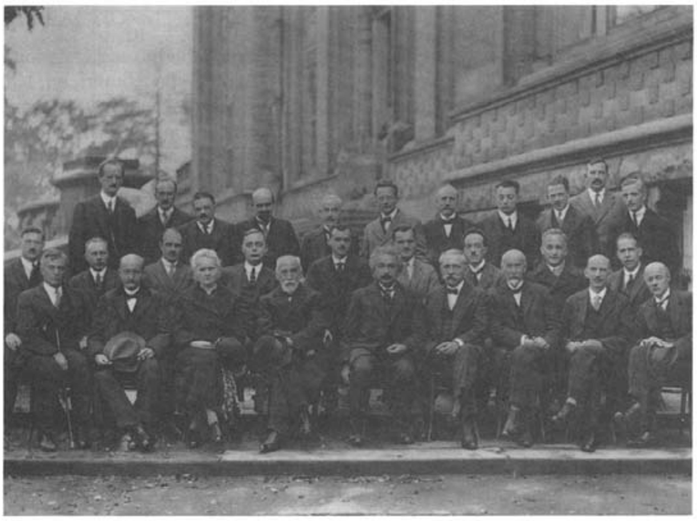
$J_I \approx M_I \cdot \Delta G_I$

$$\Delta G_{total} = \Delta G_D + \Delta G_I$$

$M_I >> M_D \rightarrow \Delta G_D >> \Delta G_I$

$\rightarrow \Delta G_I \approx 0$ Local equilibrium

How can you formulate the irreversibility in chemical reactions?



Théophile De Donder (1872–1957) (5th from the left, third row) at the historic 1927 Solvay conference. His book, *L'Affinité* was published the same year. *First row, L to R*: I. Langmuir, M. Planck, Mme Curie, H.A. Lorentz, A. Einstein, P. Langevin, Ch.E. Guye, C.T.R. Wilson, O.W. Richardson. *Second row, L to R*: P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L. de Broglie, M. Born, N. Bohr. *Third row, L to R*: A. Picard, E. Henriot, P. Ehrenfest, Ed. Herzen, Th. De Donder, E. Schrödinger, E. Verschaffelt, W. Pauli, W. Heisenberg, R.H. Fowler, L. Brillouin.

Modern Thermodynamics
D. Kondepudi
I. Prigogine
(1998)

$$dU = TdS - PdV + \sum \mu_k dn_k$$

$$dn_k = d_i n_k + d_e n_k$$

$d_i n_k =$ the change due to irreversible chemical reactions

$d_e n_k =$ the change due to exchange of matter with the exterior

$$d_e S = \frac{dU + PdV}{T} - \frac{\sum \mu_k d_e n_k}{T}$$

$$d_i S = -\frac{\sum \mu_k d_i n_k}{T} \qquad dS = d_e S + d_i S$$

Td_iS = "uncompensated heat" of Clausius for chemical reaction

Irreversibility in Chemical Reactions

$$A_{(g)} + B_{(g)} \rightleftarrows 2C_{(g)}$$

dn_A, dn_B and dn_C : change in the mole numbers

$$\frac{dn_A}{-1} = \frac{dn_B}{-1} = \frac{dn_C}{2} \equiv d\xi$$

$\xi \rightarrow$ extent of reaction

$$dS = \frac{dU + PdV}{T} + \frac{1}{T}\left(\mu_A + \mu_B - 2\mu_C\right)d\xi$$

$$dS = \frac{\left(\mu_A + \mu_B - 2\mu_C\right)}{T}d\xi > 0$$

$$A \equiv \left(\mu_A + \mu_B - 2\mu_C\right) \rightarrow \text{affinity}$$

$$\Delta\mu = 2\mu_A - \mu_B - \mu_C = -\text{Affinity}$$

→ change in chemical potential

→ *criterion for irreversible chemical reactions*

$$A_{(g)} + B_{(g)} \rightleftarrows 2C_{(g)}$$

Gaskell

$$0 \quad 0 \qquad 2$$

At any instant during the reaction,

$$G' = n_A\mu_A + n_B\mu_B + n_C\mu_C$$

where n_A, n_B, and n_C are, respectively, the numbers of moles of A, B, and C present in the reaction system at that instant.

$$n_A = n_B \qquad n_C = 2 - n_A - n_B = 2(1 - n_A)$$

$$G' = n_A\mu_A + n_A\mu_B + 2(1 - n_A)\mu_C$$

$$A_{(g)} + B_{(g)} \rightleftarrows 2C_{(g)}$$

Gaskell

$$\left(\frac{\partial G'}{\partial n_A}\right) = \mu_A + \mu_B - 2\mu_C = 0 \quad \rightarrow \text{equailibrium reaction}$$

$$\mu_A + \mu_B = 2\mu_C$$

$$\left(\frac{\partial G'}{\partial n_A}\right) = \mu_A + \mu_B - 2\mu_C > 0 \quad \rightarrow \text{backward reaction}$$

$$\mu_A + \mu_B > 2\mu_C$$

$$\left(\frac{\partial G'}{\partial n_A}\right) = \mu_A + \mu_B - 2\mu_C < 0 \quad \rightarrow \text{forward reaction}$$

$$\mu_A + \mu_B < 2\mu_C$$

Driving Force for Chemical Reactions

→ Change in chemical potentials
from products to reactants

$$\Delta\mu = \sum \mu_i^p n_i^p - \sum \mu_i^r n_i^r = -\mathit{Affinity}$$

Ideal Gases and their Mixtures

The variation of the molar Gibbs free energy of a closed system of fixed composition, with pressure at constant T,

$$dG = VdP \qquad dG = \frac{RT}{P}dP = RTd\ln P$$

$$G(P_2,T) - G(P_1,T) = RT\ln\frac{P_2}{P_1}$$

$$G(P,T) = G^o(T) + RT\ln P$$

$$G = G^o + RT\ln P$$

$G^o(T) = G(P = 1,T)$: standard Gibbs free energy

$$\mu = \mu^o + RT\ln P$$

Ideal Gases and their Mixtures

$$P_i = X_i P \rightarrow \text{Dalton's law of partial pressure}$$

For molecules of component i, the mixing process is equivalent to an isothermal expansion from an initial pressure P to a final pressure P_i.

The change in chemical potential experienced by component i can be obtained by

$$d\overline{G}_i = d\mu_i = -\overline{S}_i dT + \overline{V}_i dP = \overline{V}_i dP \quad \text{for isothermal mixing}$$

Ideal Gases and their Mixtures

$$V' = n_T \frac{RT}{P} = \left(n_1 + n_2 + \ldots + n_i + \ldots + n_c\right)\frac{RT}{P}$$

$$\overline{V}_i = \left(\frac{\partial V'}{\partial n_i}\right)_{T,P,n_j} = (1)\frac{RT}{P}$$

$$\mu_i - \mu_i^o = \int_P^{P_i} \overline{V}_i dP = \int_P^{P_i} \frac{RT}{P} dP = RT \ln \frac{P_i}{P}$$

Chemical Potential in an Ideal Gas Mixture

$$\mu_i(T,P_i) = \mu_i(T,P) + RT\ln(P_i/P)$$

$$\rightarrow \mu_i(T,P_i) = \mu_i^o + RT\ln(P_i/P)$$

$$\rightarrow \bar{G}_i = G_i^o + RT\ln P_i$$

$$\because P = 1 \rightarrow \text{standard state}$$

How do we treat non-ideal gases?

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \rightarrow \textit{van der Waals eq.}$$

$$G = G^o + RT\ln P$$

$$dG = RTd\ln f \qquad \leftarrow \textit{fugacity}$$

$$G = C(T) + RT\ln f$$

How do we define the standard state?

Non-ideal Gases

$G = G^o + RT\ln P$ $\qquad$ $G = G^o + RT\ln f$ $\qquad$ f : fugacity

The integration constant is chosen such that the fugacity approaches the pressure as the pressure approaches zero, i.e.,

$\phi = \frac{f}{p} \rightarrow 1 \text{ as } P \rightarrow 0 \qquad f = \phi p \qquad \phi : \text{fugacity coeff.}$

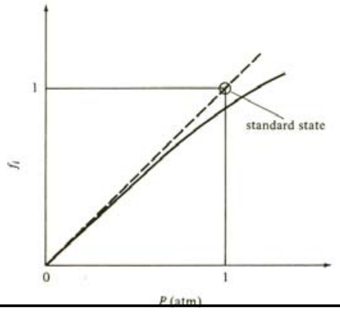


Figure 1. Standard state commonly adopted for a gas. The deviation between the two lines is exaggerated in order to present a clearer illustration.

Lupis

Standard State of Non-ideal Gases

$$G = G^o + RT\ln f$$

G^o, the Gibbs free energy of the standard state, defined as that state in which f = 1 at T.

Fugacity may be thought of as a thermodynamic pressure; it has units of pressure. (gas)

Fugacity can also be thought of as an escaping tendency. (condensed phase)

What is activity?
How is it defined?

The expression dG = RT dln f may be integrated between two states 1 and 2 to give:

$$G_2 - G_1 = RT\ln(f_2/f_1)$$

This equation applies to a pure one-component system. For a solution we must use chemical potentials,

$$\mu_i'' - \mu_i' = RT\ln\left(f_i''/f_i'\right)$$

The absolute values of the fugacities of solids and liquids cannot always be determined, but their ratios can be.

$$\mu_i'' - \mu_i' = RT\ln\left(f_i''/f_i'\right)$$

If we let one of these states be a reference state, this can be rewritten:

$$\mu_i - \mu_i^o = RT\ln\left(f_i/f_i^o\right)$$

$$a_i = f_i/f_i^o$$

$$\mu_i - \mu_i^o = RT\ln a_i \qquad \mu_i = \mu_i^o + RT\ln a_i$$

Mixtures of Ideal Gases

$\rightarrow \mu_i(T,P_i) = \mu_i^o + RT\ln(P_i/P_i^o)$

$\rightarrow \bar{G}_i = G_i^o + RT\ln P_i$

$\because P_i^o = 1 \rightarrow$ standard state

$$\mu_i = \mu_i^o + RT\ln(P_i/P_i^o)$$
$$= \mu_i^o + RT\ln P_i$$
$$= \mu_i^o + RT\ln a_i$$

Non-Ideal Pure Gas

$$G = G^o + RT\ln f$$
$$= G^o + RT\ln\left(\frac{f}{f^o}\right) \rightarrow f^o = 1$$
$$= G^o + RT\ln a$$

Mixtures of Non-Ideal Gases

$$\mu = \mu^o + RT\ln f$$
$$= \mu^o + RT\ln\left(\frac{f}{f^o}\right)$$
$$= \mu^o + RT\ln a$$

How do we treat solutions?

$\rightarrow$ *in terms of gas in equilibrium with solutions*

What is the statistical meaning of equilibrium vapor pressure of a condensed phase?

Evaporation

Find the expression for the fraction of surface atoms which have energies greater than the activation energy for evaporation, E.*

$$\frac{n_i}{N} = \frac{e^{-(\varepsilon_i / kT)}}{P_{MB}} = \frac{e^{-(\varepsilon_i / kT)}}{\sum_{i=1}^{r} e^{-(\varepsilon_i / kT)}}$$

$P \equiv \sum_{i=1}^{r} e^{-(\varepsilon_i / kT)}$: Partition function

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The energies of the atoms at the surface are quantized, and the distribution of the surface atoms among the available quantized energy levels is given as

$$n_i = \frac{N \exp\left(-E_i / kT\right)}{\sum \exp\left(-E_i / kT\right)}$$

If the quantized energy levels are spaced closely enough that the summation can be replaced by an integral, then

$$P = \int_0^\infty \exp\left(-\frac{E_i}{kT}\right) dE = kT,$$

which is thus the average energy per atom.

The fraction of surface atoms which have energies greater than the activation energy for evaporation, E^*, is

$$\frac{n_i^*}{N} = \frac{1}{kT}\int_{E^*}^\infty \exp(-E/kT)\,dE = \exp\left(-\frac{E^*}{kT}\right)$$

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equil. vapor pressure of pure A = p_A^o

equil. vapor pressure of pure B = p_B^o

mixture → $X_A,\ X_B$

What would be the equil. vapor pressure of A and B for the mixture?

$$p_A = X_A p_A^o$$
$$p_B = X_B p_B^o$$

→ *Raoult's law*

→ *applicable when the magnitudes of the A-A, B-B, and A-B bond energies in the solution are identical.*

→ *normally applicable when the concentration is high*