Biophysical Chemistry for Life Scientists

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Lecture 6

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Gibbs Free Energy (G)

- $G = H - T S$
- Extensive property of a system
- State function, e.g., $G(n, T, P)$
- T and P are particularly meaningful variables since $\Delta G_{system} \leq 0$ or W_{useful} provides a criterion for the spontaneity of a chemical or biological process at constant T and P.

Temperature and pressure dependence of G

(1) Closed system

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

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

Recall:

First Law: $dE = dQ + dW$

or $dE = dQ_{rev} + dW_{rev}$ for a reversible process

or $dE = dQ_{rev} - PdV + dW_{useful}$

$= TdS - PdV$ if no useful work

Substituting,

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

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

$$= VdP - SdT$$

From this result, it follows that for a closed system

$$(\partial G/\partial P)_{T,n} = V \quad \text{and} \quad (\partial G/\partial T)_{P,n} = -S$$

ΔG_{system} due to changes in temperature at constant P

$$(\partial G/\partial T)_{P,n} = -S$$

$$\Delta G = -\int_{T_{initial}}^{T_{final}} S(T, P)\, dT$$

ΔG_{system} due to changes in pressure at constant T

$$(\partial G/\partial P)_{T,n} = V$$

$$\Delta G = \int_{P_{initial}}^{P_{final}} V(T, P)\, dP$$

(2) Open system

$$G(n, T, P)$$

However, because G is an extensive property, we could write $G(n, T, P) = n\,\overline{G}\,(T,P)$. That is, the Gibbs free energy of the system must be proportional

to the n, the number of moles of the substance, as well as T and P. $\overline{G}$ (T, P) is the Gibbs free energy per mole of the substance at temperature T and pressure P. The molar free energy of a substance at T and P is usually referred to as the chemical potential of the substance at that temperature and pressure, and is given the symbol μ (T,P).

So, at a given T and P,

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

and

$$dG = (\partial G/\partial T)_{P,n}\, dT + \partial G/\partial P)_{T,n}\, dP \;+ \mu\,(T, P)\, dn$$

$$= - S\,(T, P)\, dT \;+\; V\,(T, P)\, dP \;+ \mu\,(T, P)\, dn$$

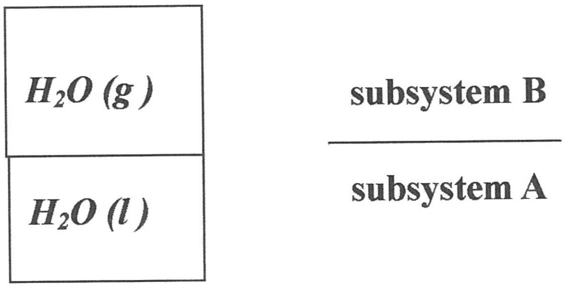
$$= \;- S\, dT \;+\; V\, dP \;+\; \mu\, dn$$

Note that the chemical potential μ (T, P) is an intensive property of the system, as it is the molar free energy of the substance in the system.

Chemical potential is a powerful concept!

We now illustrate the power of the chemical potential by way of a simple example: Phase equilibrium

Consider a closed vessel containing water vapor in equilibrium with liquid water.



total system closed
but each phase open

If the system is in internal equilibrium,

$$T^A = T^B$$

superscript to denote phase

$$P^A = P^B = P$$

P^B is the vapor pressure of the liquid at temperature T

Since T and P are constant, we can write

$$dG^A = \mu^A(T, P)\, dn^A$$

$$dG^B = \mu^B(T, P)\, dn^B$$

Closed system: P, V work possible, but no other work.

At equilibrium,

$$dG = 0 = dG^A + dG^B = \mu^A(T, P)\, dn^A + \mu^B(T, P)\, dn^B$$

But $dn^A + dn^B = 0$ since $n_{total} = n^A + n^B$

or $dn^A = - dn^B$

So,

$$\mu^A(T, P) = \mu^B(T, P)$$

Thus when two phases are in equilibrium in a one-component closed system, the chemical potential of the substance in both phases must be equal at the equilibrium T and P.

We have derived an important result, because this relationship enables us to relate the chemical potential of the gas or vapor to the chemical potential of the liquid at equilibrium at T and P. In a moment, we shall take advantage of this result to obtain the chemical potential of the liquid.

Before I proceed to the chemical potential of the liquid, I would like to show that dE = T dS – P dV for the entire system if it is in internal equilibrium. Recall

$$dE^A = T^A dS^A - P^A dV^A + \mu^A\, dn^A$$

$$dE^B = T^B dS^B - P^B dV^B + \mu^B\, dn^B$$

[It turns out that the chemical potential $\mu = (\partial E/\partial n)_{V,S} = (\partial H/\partial n)_{P,S}$ as well!]

Adding,

$$dE^A + dE^B = T^A dS^A + T^B dS^B - P^A dV^A - P^B dV^B$$

$$+ \mu^A\, dn^A + \mu^B\, dn^B$$

or $$\underset{dE}{(dE^A + dE^B)} =$$

$$\underset{T\,dS}{T\,(dS^A + dS^B)} \underset{-P\,dV}{- P(dV^A + dV^B)} + \underset{0}{\mu^A\, dn^A + \mu^B\, dn^B}$$

or $$dE = T\,dS - P\,dV$$

since $T^A = T^B$

$P^A = P^B$ for two phases in equilibrium

$\mu^A = \mu^B$

As I noted earlier, the outcome of the above analysis should enable us to relate the chemical potential of the liquid to the chemical potential of the vapor or gas at equilibrium at T and P.

- **Chemical potential of vapor**

For convenience, the chemical potential of a gas or vapor is always referred to that of the pure gas at 1 atm (standard pressure, P°) at the same temperature. This reference is called the standard state. From

$$\Delta G = \int_{P_{initial}}^{P_{final}} V(T, P)\, dP$$

and assuming ideal behavior for the vapor, we obtain

$$\mu^{vapor}(T, P^{vapor}) - \mu^{\circ}_{vapor}(T, P^{\circ}) = \int_{P^{\circ}}^{P^{vapor}} \overline{V}(T, P)\, dP$$

$$= \int_{P^\circ}^{P^{vapor}} (RT/P)\, dP = RT \ln (P^{vapor}/P^\circ)$$

where $\overline{V} = RT/P$ is the molar volume of the gas, and P^{vapor} is the vapor pressure of the liquid at temperature T. So

$$\mu^{vapor}(T, P^{vapor}) = \mu^\circ_{vapor}(T, P^\circ) + RT \ln (P^{vapor}/P^\circ)$$

where $\mu^\circ_{vapor}(T, P^\circ)$ is the chemical potential, or free energy per mole, of pure vapor at temperature T and standard pressure of 1 atmosphere (P°).

So from $\mu^{liquid}(T, P^{liquid}) = \mu^{vapor}(T, P^{vapor})$

$$T^{liquid} = T^{vapor}$$

$$P^{liquid} = P^{liquid}$$

we obtain

$$\mu^{liquid}(T, P^{liquid}) = \mu^\circ_{vapor}(T, P^\circ) + RT \ln (P^{vapor}/P^\circ)$$

Note that the liquid is in equilibrium with its vapor pressure at each temperature in this analysis, i.e., the liquid is under a different pressure at each temperature. One could, of course, add a foreign gas that is insoluble in the liquid to bring the total pressure on the liquid to 1 atm at each temperature. There would be a small correction to the vapor pressure of the liquid, or the partial pressure of the liquid vapor in the gas phase.

Gibbs Free Energy, dG and ΔG for a multicomponent system

The Gibbs Free Energy G is an extensive variable, so for a multicomponent system at temperature T and pressure P

↖ total pressure

$$G_{system}(T,P) = \sum_{\substack{i \\ \text{all components}}} G_i = \sum_{i} \mu_i(T,P)\, n_i$$

and dG_{system}

$$= \sum_{\substack{i \\ \text{all components}}} \left\{ n_i \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\, n_1,\, n_2 \ldots} dT + n_i \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\, n_1,\, n_2 \ldots} dP + \mu_i(T,P)\, dn_i \right\}$$

$$= \left(\frac{\partial G_{system}}{\partial T}\right)_P + \left(\frac{\partial G_{system}}{\partial P}\right)_T + \sum_{\substack{i \\ \text{all components}}} \mu_i \, (T,P) dn_i$$

A simple multi-component system: Chemical equilibrium for a homogeneous gaseous reaction

Consider the following homogeneous gaseous reaction involving the ideal gases A, B, C, and D at T and P:

$$\underline{a}\, A + \underline{b}\, B \rightarrow \underline{c}\, C + d\, D$$

At equilibrium, we could write

$$dG = \sum_{\substack{i \\ \text{chemical species}}} \mu_I \, dn_i = 0$$

But $dn_i = \pm \nu_i \, d\xi$ **where** $\xi \equiv$ **extent of reaction**

ν_i **≡ stoichiometric coefficient for the species i**

+ for products

- for reactants

Therefore,

$$\left(\sum_{\substack{i \\ products}} \nu_i \mu_i - \sum_{\substack{j \\ reactants}} \nu_j \mu_j \right) d\xi = 0$$

or for above reaction:

$$\underline{c}\ \mu_C(T,P_C) + \underline{d}\ \mu_D(T,P_D) - \underline{a}\ \mu_A(T,P_A) - \underline{b}\ \mu_B(T,P_B) = 0$$

where I have specified the partial pressures of the gases at chemical equilibrium.

Now if the gases behave ideally,

$\mu_A(T, P_A)$ only, i.e., depends on the partial pressure of the gas in the mixture only, and independent of P_T, and so on, and we may write

$$\mu_A(T, P_A) = \mu^\circ_A(T, P^\circ) + RT \ln (P_A/P^\circ)$$

$$\mu_B(T, P_B) = \mu^\circ_B(T, P^\circ) + RT \ln (P_B/P^\circ)$$

$$\mu_C(T, P_C) = \mu^\circ_C(T, P^\circ) + RT \ln (P_C/P^\circ)$$

$$\mu_D(T, P_D) = \mu^\circ_D(T, P^\circ) + RT \ln (P_D/P^\circ)$$

Substituting,

$$\underline{c}\,\mu^\circ_C(T) + \underline{d}\,\mu^\circ_D(T) - \underline{a}\,\mu^\circ_A(T) - \underline{b}\,\mu^\circ_B(T)$$

$$+\,\underline{c}\,RT\ln(P_C^{eq}/P^\circ) + \underline{d}\,RT\ln(P_D^{eq}/P^\circ)$$

$$-\;\underline{a}\,RT\ln(P_A^{eq}/P^\circ) - \underline{b}\,RT\ln(P_B^{eq}/P^\circ) \quad = 0$$

where explicit P° dependence of the standard chemical potentials has been removed (1 atm always), and "eq" has been added to the partial pressures of the gases to denote that we are referring to the partial pressures at chemical equilibrium.

Final result:

$$\underline{c}\,\mu^\circ_C(T) + \underline{d}\,\mu^\circ_D(T) - \underline{a}\,\mu_A(T) - \underline{b}\,\mu_B(T) =$$

$$\Delta G^\circ(T) = -RT\ln\left(\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}\right)_{eq} \underbrace{\boxed{+RT\ln\left(\frac{(P^o)^c(P^o)^d}{(P^o)^a(P^o)^b}\right)}}_{0}$$

Since $\dfrac{(P_C{}^c)(P_D{}^d)}{(P_A{}^a)(P_B{}^b)} = K_{P.}$

$$\Delta G^\circ(T) \quad = \quad -RT\ln K_P$$

where

$$\Delta G^\circ\,(T) = \underline{c}\;\mu^\circ_C(T) + \underline{d}\;\mu^\circ_D(T) - \underline{a}\;\mu^\circ_A(T) - \underline{b}\;\mu^\circ_B(T)$$

= standard free energy change

i.e., free energy change for the reaction:

$$\underline{a}\,A(gas,\ pure,\ ideal,\ 1\ atm,\ T) + \underline{b}\,B\,(gas,\ pure,\ ideal,\ 1\ atm,\ T)$$

$$\rightarrow \underline{c}\,C(gas,\ pure,\ ideal,\ 1\ atm,\ T) + \underline{d}\,D(gas,\ pure,\ ideal,\ 1\ atm,\ T).$$

Above, we have derived the result when the system has reached chemical equilibrium. In general,

$$\Delta G(T,\underset{=P_T}{P}) = \Delta G^\circ(T) + RT\ln Q,\ \text{where}\ Q \equiv \text{equilibrium quotient}$$

where $Q = \dfrac{(P_C{}^c)(P_D{}^d)}{(P_A{}^a)(P_B{}^b)}$ under the conditions of system.

If $\Delta G > 0$, reaction will proceed to left

$\Delta G < 0$, reaction will proceed to right as written

and $\Delta G = 0$, $Q = K_P$ and reaction has reached equilibrium .

Different Ways of Expressing the equilibrium quotient Q

- **Q_X and K_X**

$$Q_P = \frac{P_C^{\,c}\, P_D^{\,d}}{P_A^{\,a}\, P_B^{\,b}}$$ subscript p to denote partial pressures

If component gases follow ideal behavior, then

$$P_C = P_T \cdot X_C \qquad P_A = P_T \cdot X_A$$

$$P_D = P_T \cdot X_D \qquad P_B = P_T \cdot X_B$$

$$\therefore Q_P = \underbrace{\left(\frac{X_C^{\,c}\, X_D^{\,d}}{X_A^{\,a}\, X_B^{\,b}}\right)}_{Q_X} P_T^{(c+d-a-b)} = Q_X P_T^{(c+d-a-b)}$$

$$\therefore \Delta G(T,P) = \Delta G^\circ(T) + RT \ln \underset{\uparrow \left(\frac{P_T}{P^\circ}\right)^{c+d-a-b}}{P_T^{\,(c+d-a-b)}} + RT \ln Q_X$$

and at equilibrium

$$\Delta G^{\circ}(T,P) = -RT\ln\left(P^{c+d-a-b}\right) \qquad - RT\ln K_X$$

where $K_X = \left(\frac{X_C{}^{\underline{c}} X_D{}^{\underline{d}}}{X_A{}^{\underline{a}} X_B{}^{\underline{b}}}\right)_{eq}$

Define $\Delta G^{\circ}(T) + RT\, ln\, P^{c+d-a-b} = \Delta G^{\circ\prime}(T,P)$

where $\Delta G^{\circ\prime}(T,P)$ refers to the free energy change for reaction:

$$\underline{a}\,A\ (gas,\ pure,\ ideal,\ P) + \underline{b}\ B\ (gas,\ pure,\ ideal,\ P)$$
$$\rightarrow \underline{c}\ C\ (gas,\ pure,\ ideal,\ P) + dD\ (gas,\ pure,\ ideal,\ P)$$

- **<u>Q_C and K_C</u>**

Return to $Q_P = \left(\frac{P_C{}^{\underline{c}}\ P_D{}^{\underline{d}}}{P_A{}^{\underline{a}}\ P_B{}^{\underline{b}}}\right)$

For ideal gases, $P_i = \frac{n_i RT}{V} = C_i RT$

so we may rewrite Q_P as

$$\left(\frac{C_C{}^{\underline{c}}\ C_D{}^{\underline{d}}}{C_A{}^{\underline{a}}\ C_B{}^{b}}\right) RT^{(c+d-a-b)} = Q_C RT^{(c+d-a-b)}$$

and

$$\Delta G(T) = \Delta G^{\circ}(T) + RT\, ln(RT)^{(c+d-a-b)} + RT\, ln\, Q_C.$$

At equilibrium,

$$\Delta G^{\circ}(T) = -RT\ln(RT)^{c+d-a-b} - RT\ln K_C$$

where $$K_C = \left(\frac{C_C^{\underline{c}}\,C_D^{\underline{d}}}{C_A^{\underline{a}}\,C_B^{\underline{b}}}\right)_{eq}.$$

Define $\Delta G^{\circ}(T) + RT\ln(RT)^{c+d-a-b} \equiv \Delta G^{\circ}(T)''$

then, $\Delta G^{\circ}(T)''$ **refers to the free energy change for the following reaction:**

$$\underline{a}\,A\,(T,\ \textit{ideal gas, pure, 1 mole/liter})$$
$$+\underline{b}\,B(T,\ \textit{ideal gas, pure, 1 mole/liter})$$
$$\longrightarrow \underline{c}\,C(T,\ \textit{ideal gas, pure, 1 mole/liter})$$
$$+\underline{d}\,D(T,\ \textit{ideal gas, pure, 1 mole/liter})$$

So, depending on the units used to express equilibrium quotient, ΔG°'s derived from equilibrium constants (K_P, K_X, K_C) refer to different standard conditions.

Chemical Equilibria for Ideal Liquid and Solid Solutions

- **What is an ideal solution?**

Ideal behavior in a gas results when there are no intermolecular forces between gas molecules. However, such a definition of ideal behavior would be unrealistic for any condensed phase. Instead, the ideality concept for liquid and solid solutions stipulates complete uniformity in all intermolecular interactions. It turns out that an equivalent definition of an ideal solution requires that the "escaping tendency" of each component, measured by the partial vapor pressure, be proportional to the mole fraction of that component in the solution. It is helpful to look at this concept from a molecular point of view. Consider an ideal solution of A & B. The definition of ideality implies that a molecule of A in the solution will have the same tendency to escape

into the vapor whether it is surrounded entirely by other A molecules, entirely by B molecules, or partly by A and partly by B molecules. This means that the intermolecular forces between A and A, A and B, and B and B are all the same, i.e., there is uniformity in all intermolecular interactions.

Some examples of an ideal solution are:

(1) Mixture of isotopes;

(2) Molecules that are closely similar chemically and in shape;

e.g. ethylene bromide and proplylene bromide,
benzene and toluene,
n-hexane and n-heptane,

(molecules need to be of similar size and shape, similar dipole moments and electric quadupole moments, similar electronic structure)

- **Raoult's Law**

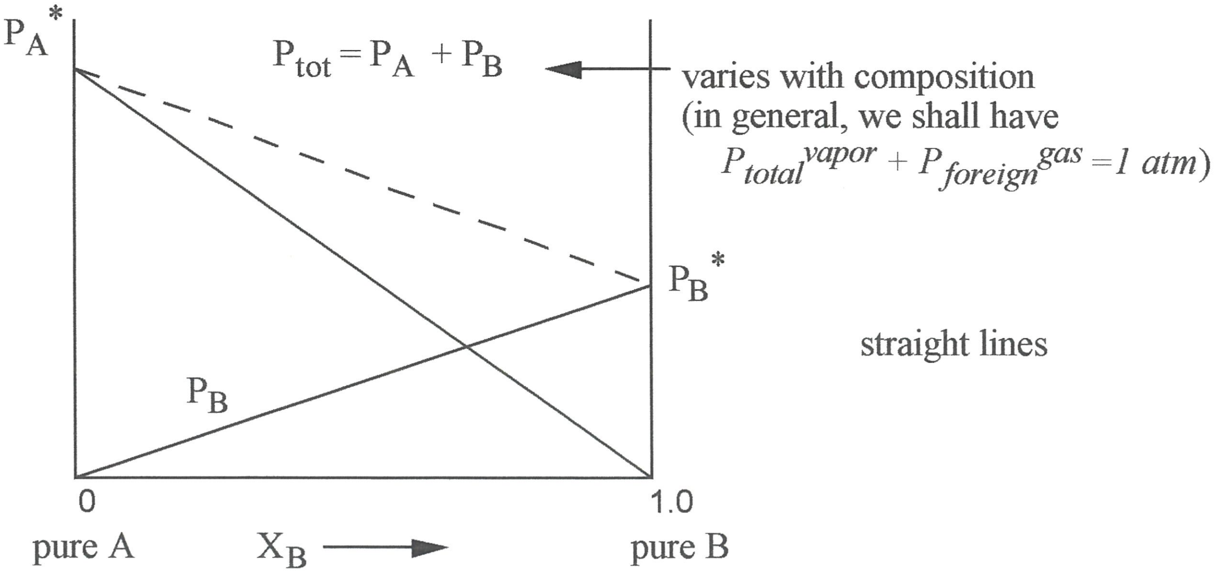
If a solution is ideal, the partial vapor pressure of any of its components, such as A, is equal to the product of

the mole fraction of the substance and the vapor pressure of the pure liquid A. This is Raoult's Law, and is mathematically expressed as

$$P_A(T) = X_A P_A^*(T)$$

where $P_A(T)$ is the vapor pressure of A above the ideal solution, X_A is the mole fraction of A in the solution, and $P_A^*(T)$ is the vapor pressure of pure liquid A at temperature T.

- **Typical Raoult-Law behavior of vapor pressures.**



- **Chemical potentials of components in an ideal solution**

Consider a two component system of an ideal solution of A and B in equilibrium with their vapors. Assume ideal behavior of the vapor. Then

$$\mu_A^{solution}(T) = \mu_A^{vap}(T) = \mu_A^{\circ\, vap}(T) + RT\, ln\, P_A^{vap}$$

and

$$\mu_B^{solution}(T) = \mu_B^{vap}(T) = \mu_B^{\circ\, vap}(T) + RT\, ln\, P_B^{vap}$$

Solution ideal $\Rightarrow$ apply Raoult's Law,

Then

$$\mu_A^{solution}(T) = \mu_A^{\circ\, vap}(T) + RT\, ln\, X_A P_A^*$$

$$\mu_B^{solution}(T) = \mu_B^{\circ\, vap}(T) + RT\, ln\, X_B P_B^*$$

or

$$\mu_A^{solution}(T) = \underbrace{\mu_A^{\circ\, vap}(T) + RT \ln\left(P_A^*/P^\circ\right)}_{\mu_A^{\circ'}(T)} + RT \ln X_A$$

$$\mu_B^{solution}(T) = \underbrace{\underbrace{\mu_B^{\circ\,\text{vap}}}_{\substack{\text{pure gases}\\ \text{at 1 atm}}}(T) + RT\ln\left(P_B^*/P^\circ\right)}_{\mu_B^{\circ\prime}(T)} + RT\ln X_B \quad \boxed{\boldsymbol{P^\circ = 1\ atm}}$$

Redefining standard states

$$\mu_A^{solution}(T) = \mu_A^{\circ\prime}(T) + RT\,ln\,X_A$$

$$\mu_B^{solution}(T) = \mu_B^{\circ\prime}(T) + RT\,ln\,X_B$$

Chemical Potential of a Solute in Solution

In the previous example of an ideal binary solution of two completely miscible components A and B, one does not have to distinguish between solvent and solute. Supposedly, the 烞olvent” and 烞olute” are sufficiently similar that this distinction is unnecessary. But for most solutions, this isn掐 the case. We now treat this more general case.

- **Henry Law**

In a very dilute solution of B (solute) in A (solvent), each B molecule is completely surrounded by A molecules, and therefore the partial vapor pressure of B in this uniform environment is also proportional to the mole fraction X_B, but the proportionality constant is no longer P_B^*. We write

$$P_B^{vap} = k_B^H X_B \qquad \textbf{(infinite dilution limit)}$$

where $k_B^H \equiv$ Henry's Law constant for solute B. Such a system is clearly <u>not</u> ideal in the sense mentioned earlier for an <u>ideal solution</u>. However, for the solvent A,

$$P_A^{vap} = P_A^* X_A$$

since A is an <u>ideal</u> solvent when the concentration of B is small.

So for this binary solution,

$$\mu_A^{solution}(T) = \mu_A^{solvent}(T) = \mu_A^{\circ'}(T) + RT\,ln X_A$$

$$\mu_B^{solution}(T) = \mu_B^{solute}(T) = \mu_B^{\circ'}(T) + RT\,ln X_B$$

↑ **infinite dilution limit**

where

$$\mu_A^{\circ'}(T) = \mu_A^{\circ\ vap}(T) + RT\,ln\left(\frac{P_A^{*}}{P^{\circ}}\right)$$

$P^{\circ} = 1\ atm$

$$\mu_B^{\circ'}(T) = \mu_B^{\circ\ vap}(T) + RT\,ln\left(\frac{k_B^{H}}{P^{\circ}}\right)$$

Instead of mole fraction for B, X_B **is usually converted to concentration units.**

<u>Molarity</u> = # of moles of B /1 liter of solution

$$C_B = \frac{n_B}{1000\ ml\ of\ solution}$$

Now $X_B = \dfrac{n_B}{n_A + n_B}$

$n_A = (1000\rho - C_B M_B)/M_A$ **<u>in 1000 ml of solution</u>**

ρ = density of solution; M_A, M_B molecular weights of A and B respectively.

$n_B = c_B$ in 1000 ml of solution

so that

$$X_B = \frac{n_B}{n_A + n_B} = \frac{c_B}{(1000\rho - C_B M_B)/M_A + C_B}$$

In dilute solutions,

$\rho \rightarrow \rho_A$ density of solvent

$(C_B M_A - C_B M_B) << 1000\rho$

$$\therefore X_B \sim \frac{C_B M_A}{1000\rho_A}$$

or X_B is proportional to C_B!

Molality = # of moles of B / 1000 grams of solvent.

$$m_B = \frac{n_B}{1000 \text{ grams of } A}$$

Now $$X_B = \frac{n_B}{n_A + n_B}$$

$n_B = m_B$ in 1000 grams of solvent

$$n_A = \frac{1000}{M_A}$$ **in 1000 grams of solvent**

so that $$X_B = \frac{m_B}{(1000/M_A) + m_B}$$

In dilute solutions,

$$M_A m_B << 1000$$

$$X_B \to \frac{m_B M_A}{1000}$$

or X_B is proportional to m_B!

<u>So</u>

$$\underset{(solute)}{\mu_B^{solution}} = \mu_B^{\circ\prime}(T) + RT\,ln\,X_B$$

$$= \mu_B^{\circ\prime}(T) + RT\,ln\left(\frac{M_A}{1000\rho_A}\right)C_B$$

$$= \underbrace{\mu_B^{\circ\prime}(T) + RT\ln\left(\frac{M_A}{1000\rho_A}C_B^{\circ}\right)}_{\mu_B^{\circ\prime\prime}(T)} \qquad + RT\ln\frac{C_B}{C_B^{\circ}}$$

where $C_B^{\circ} = 1$ mole / liter

new standard state

chemical potential of solute B in solvent A at concentration of 1 mole/liter (1 M) at temperature T and pressure 1 atm, but environment identical to that B in solution at infinite dilution.

or

$$\underset{(solute)}{\mu_B^{solution}} = \mu_B^{\circ'}(T) + RT\,ln\,X_B$$

$$= \mu_B^{\circ'}(T) + RT\,ln\left(\frac{M_A}{1000}\right)m_B$$

$$= \underbrace{\mu_B^{\circ'}(T) + RT\ln\left(\frac{M_A}{1000}\right)m_B^{\circ}}_{\mu_B^{\circ''}(T)} \qquad + RT\ln\frac{m_B}{m_B^{\circ}}$$

where $m_B^{\circ} = 1\ molal = 1\underline{m}$

new standard state

chemical potential of solute B in solvent A at concentration of 1 molal (1 M) at temperature T and pressure 1 atm, but identical to B in the solution at infinite dilution.