

Chemistry BC3252y: Part VI  
**Systems of variable composition**  
 (the formal tools)



Heretofore, **n** has not been a **variable**  
 (except to define to overall scale)

But if **composition** can vary freely,  
 instead of  $G(p, T)$  we have  **$G(p, T, n_1, n_2, \dots)$** .

Since  $G$  is a state function its total differential is

$$dG = \left( \frac{\partial G}{\partial p} \right)_{T, n_j} dp + \left( \frac{\partial G}{\partial T} \right)_{p, n_j} dT + \left( \frac{\partial G}{\partial n_1} \right)_{T, p, n_j \neq n_1} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T, p, n_j \neq n_2} dn_2 + \dots$$

Observe carefully what is being held constant:  
 in the first two derivatives, **all  $n_i$**  (plus  $p$  or  $T$ )  
 in the rest **all  $n_i$  except the one being varied**  
 (Atkins denotes this as  **$n'$** ) plus  $p$  and  $T$ .

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**Chemical potential**

Define a new quantity  $\mu_i$  called **chemical potential**

$$\mu_i \equiv \left( \frac{\partial G}{\partial n_i} \right)_{p, T, n'}$$

Then  $dG = V dp - S dT + \sum \mu_k dn_k$

where the sum is taken over all species.

A fundamental equation for an **open system**.

What is  $\mu_k$ ?

For a pure substance  $G = nG_m$ , so  $\mu_k = G_m$

The chemical potential of a pure substance  
 is its **molar Gibbs free energy**.

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**Example: phase transition**

Consider a system with two pure phases,  $\alpha$  and  $\beta$

$$dG = V dp - S dT + \mu_\alpha dn_\alpha + \mu_\beta dn_\beta$$

If  $p$  and  $T$  are constant,  $dG = \mu_\alpha dn_\alpha + \mu_\beta dn_\beta$

When molecules go from  $\beta$  to  $\alpha$ ,  $dn_\alpha = -dn_\beta$

$$dG = (\mu_\alpha dn_\alpha - \mu_\beta dn_\alpha) = (\mu_\alpha - \mu_\beta) dn_\alpha$$

If the process is spontaneous:  $dG < 0$

If  $dn_\alpha > 0$ , then  $(\mu_\alpha - \mu_\beta) < 0$ ; so  $\mu_\beta > \mu_\alpha$

**$n_\alpha$  will increase if its chemical potential ( $\mu_\alpha$ ) is lower.**

**Molecules will move spontaneously into  
 the phase with the lower chemical potential.**

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## Why “chemical potential”?

Molecules move spontaneously towards the phase with the lower chemical potential.

Like  $p$  and  $T$ ,  $\mu$  is an **intensive property**.

$\mu$ ,  $p$  and  $T$  play similar roles:

When there is a **pressure** gradient, matter flows towards the region of lower pressure.

When there is a **temperature** gradient, heat flows towards the region of lower temperature.

When there is a **chemical potential** gradient, matter moves towards the region of lower  $\mu$ .

At equilibrium,  $p$ ,  $T$  and **all** the  $\mu_k$  values (different for each  $k$ ) are **uniform** throughout the system.

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## Chemical potential: Pure ideal gas

$$dG = V dp - S dT$$

So for a pure substance

$$d\mu = dG_m = V_m dp - S_m dT$$

If  $T$  is constant,  $d\mu = V_m dp$   
for an ideal gas  $V_m = RT/p$

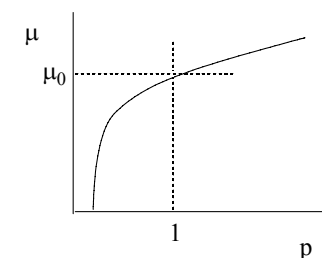
Integrate:

$$\mu = \mu^\circ + RT \ln p$$

where  $\mu^\circ = \mu$  when  $p = p^\circ$

and  $p^\circ = \text{one (atm or bar)}$ .

**If  $p$  falls,  $\mu$  falls.**



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## Why “chemical potential”?

In a system at **equilibrium** the chemical potential of  $j$  is the same everywhere, for example  $\mu_{j,\ell} = \mu_{j,g}$ .

When there is an imbalance in chemical potential, molecules move towards the region of lower  $\mu$  until the  $\mu$ 's are balanced.

If  $\mu_{j,\ell} < \mu_{j,g}$  then  $j$  molecules in gas will condense: this lowers  $p$ , so it lowers  $\mu_{j,g}$

The process continues until  $\mu_{j,\ell} = \mu_{j,g}$  then the system is in **equilibrium**.

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## Relating chemical potential to the other energies (U, H, and A)

$$dG = V dp - S dT + \sum \mu_k dn_k$$

$$G = H - TS \rightarrow dH = dG + TdS + SdT$$

$$dH = V dp + TdS + \sum \mu_k dn_k$$

$$dH = (\partial H / \partial p)_{S,n} dp + (\partial H / \partial S)_{p,n} dS + \sum (\partial H / \partial n_k)_{p,S,n'} dn_k$$

Equating coefficients,  $\mu_k = (\partial H / \partial n_k)_{p,S,n'}$

Similar result for each of the energies:

$$\mu_k = (\partial U / \partial n_k)_{V,S,n'} = (\partial A / \partial n_k)_{V,T,n'}$$

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## Fundamental equations for open systems

$$dG = +V dp - S dT + \sum \mu_k dn_k$$

$$dH = +V dp + TdS + \sum \mu_k dn_k$$

$$dA = -p dV - S dT + \sum \mu_k dn_k$$

$$dU = -p dV + TdS + \sum \mu_k dn_k$$

sums go over all species k

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## Additivity relation for G

$$dU = -p dV + T dS + \sum \mu_k dn_k$$

differentials are all of **extensive** properties

$$U = nU_m, V = nV_m, S = nS_m, n_k = nX_k$$

If we scale system holding (p, T, X<sub>k</sub>) constant, then

$$dU = U_m dn, dV = V_m dn, dS = S_m dn, dn_k = X_k dn$$

$$U_m dn = -pV_m dn + TS_m dn + \sum \mu_k dX_k dn$$

$$= (-pV_m + TS_m + \sum \mu_k X_k) dn$$

$$\text{thus } U_m = (-pV_m + TS_m + \sum \mu_k X_k)$$

$$U_m + pV_m - TS_m = + \sum \mu_k X_k$$

But  $U + pV - TS = G!$  Therefore  $G_m = + \sum \mu_k X_k$

Multiply through by n:  $G = + \sum \mu_k n_k$

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## Additivity relation: $G = \sum n_k \mu_k$

The total Gibbs free energy for the system is the sum (over all species) of the moles of each species times its chemical potential.

For a system composed of separate **pure** substances, this might seem obvious:

$$G = n_A G_m(A) + n_B G_m(B) + \dots$$

But the derivation proves this is also true in **mixtures**.

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## The Gibbs-Duhem equation

$$dG = + \sum \mu_k dn_k + \sum n_k d\mu_k$$

$$dG = V dp - S dT + \sum \mu_k dn_k$$

$$\sum n_k d\mu_k = V dp - S dT \quad \text{Gibbs-Duhem equation.}$$

(p, T, and  $\mu_k$ ) are not independent of one another!

Example. Suppose we have pure liquid water in equilibrium with its vapor at fixed (p, T)

$$\text{The GD equation says } n_l d\mu_l + n_g d\mu_g = 0$$

*Put a little salt in the liquid.*

This makes  $\mu_l$  change: it decreases, due to mixing.

This implies that  $\mu_g$  must change too, even though

there is no salt there. **How? The vapor pressure falls.**

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## Partial molar quantities

For a **pure substance**,  $G = nG_m$ , so when temperature and pressure are fixed,  $\mu_k \equiv (\partial G / \partial n_k)_{p,T,n'} = G_{m,k}$

Chemical potential is the **molar Gibbs free energy**

In a **mixture (solution)** the presence of other substances in general changes the environment experienced by k,

$$\text{so } \mu_k \neq G_{m,k}$$

Chemical potential is the **partial molar Gibbs free energy**.

Partial molar quantities are similarly defined

for any **extensive** variable Z:  $Z_i \equiv (\partial Z / \partial n_i)_{p,T,n'}$

All extensive properties are additive:  $Z = +\sum n_k Z_k$

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## Partial molar quantities

For any **extensive** variable Z,  $Z_i \equiv (\partial Z / \partial n_i)_{p,T,n'}$

Additivity:  $Z = \sum n_k Z_k$       Verify: take  $(\partial / \partial n_k)_{p,T,n'}$

Gibbs-Duhem equation says  $\sum n_k d\mu_k = V dp - S dT$

$$\sum n_k d\mu_k = (\sum n_k V_k) dp - (\sum n_k S_k) dT$$

$$\sum n_k d\mu_k - (\sum n_k V_k) dp + (\sum n_k S_k) dT = 0$$

$$\sum n_k \{d\mu_k - V_k dp + S_k dT\} = 0$$

The only way this can be true for any n is that

**all coefficients must be zero:**  $\{d\mu_k - V_k dp + S_k dT\} = 0$

$$d\mu_k = V_k dp - S_k dT.$$

Compare (for pure gas):  $dG_m = V_m dp - S_m dT$

Same equation holds, now for partial molar quantities!

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## Partial molar volumes

Partial molar **volume**  $V_k \equiv (\partial V / \partial n_k)_{p,T,n'}$

Consider a **mixture** of two liquids 1 and 2:

$$V_1 = (\partial V / \partial n_1)_{p,T,n_2} \text{ and } V_2 = (\partial V / \partial n_2)_{p,T,n_1}$$

Are these the same as the **molar** volumes

of these pure liquids  $V_k^*$ ? [ $*$  = pure]

**No!** Volumes are **not** simply additive:

When you mix 100 mL water and 100 mL alcohol, the resulting solution has volume ~190 mL.

$$V \neq n_1 V_1^* + n_2 V_2^*$$

Some books use a special symbol to distinguish a partial molar quantity from a molar quantity.

Atkins does not: you must infer from the context.

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## $V_k \equiv (\partial V / \partial n_k)_{p,T,n'}$ *What does this really mean?*

Start with a solution at (T, p, and X),  
for example a water-alcohol mixture.

Add a *very* small quantity of water,  $\delta n_w$ .

The volume changes by an amount  $\delta V$ .

$\delta V / \delta n_w$  is the partial molar volume.

**Alternatively**, start with an infinitely large sample of the same solution at (T, p, and X).

Add one mole of water:

the increase in volume is the partial molar volume.

Water and alcohol are an extreme example:

often the molar volumes and the partial molar volumes of two liquids in a mixture are nearly the same.

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## Determining partial molar volumes

Make a series of mixtures of water and alcohol at various mole fractions, and measure  $V_m = V/n$ , where  $n$  is the total number of moles. **Plot  $V_m$  vs.  $X$ .**

At  $X_e = 0$ ,  $V_m = V_{m,w}^*$  and at  $X_e = 1$ ,  $V_m = V_{m,e}^*$

In between, not a straight line, but a curve.

Additivity says  $V = n_1V_1 + n_2V_2 = n(X_1V_1 + X_2V_2)$ .

But  $X_1 = 1 - X_2$ , so  $V_m = V_1 + X_2(V_2 - V_1)$ .

If the  $V_k$ 's were constant, this would be a straight line with  $V_m$  (at  $X_2 = 0$ ) =  $V_1^*$  and  $V_m$  (at  $X_2 = 1$ ) =  $V_2^*$ .

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## Determining partial molar volumes

For one mole,  $V = V_1 + X_2(V_2 - V_1)$

$V_1$  and  $V_2$  vary with  $X_2$ , so

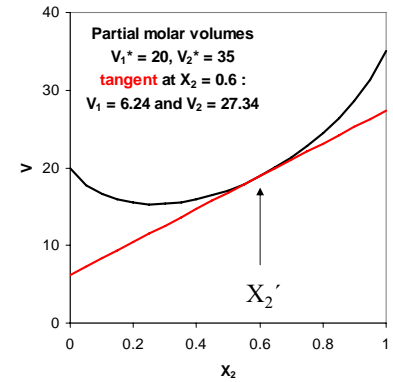
$V$  vs.  $X$  is not a straight line.

Take the values of  $V_1$  and  $V_2$  at some arbitrary  $X_2 (= X_2')$ ,

draw a straight line with intercept  $V_1$  and slope  $(V_2 - V_1)$ .

That line is tangent to the curve  $V_m$  vs.  $X_2$  at  $X_2'$ , and crosses  $V_1$  when  $X_2 = 0$  and  $V_2$  when  $X_2 = 1$ .

This diagram exaggerates typical curvature!



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## Determining partial molar volumes

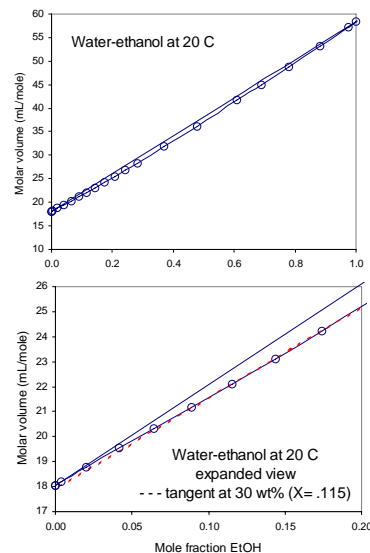
$$V_m = V_1 + X_2(V_2 - V_1)$$

**Result:** The quantities  $V_1$  and  $V_2$  are the **intercepts** of the **tangent** to the  $V_m$  vs  $X$  curve at each  $X$ .

**Data:** ethanol-water at 20°C. from *International Critical Tables* Vol. 3, p, 117.

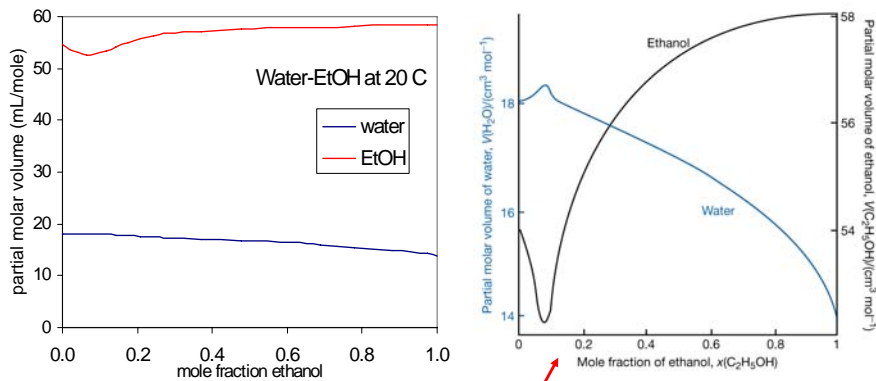
$V$  is not linear in  $X$ , but the deviations are not very large.

Tangents at a point - - - generate partial molar volumes (via spreadsheet)



Microsoft Excel - partialmolar.xls													
File Edit View Insert Format Tools Data Window Help SmartList To Go Acrobat													
=G14:H14*F14													
A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	Water-alcohol mixtures at 20 C				molar	Slope determined from two adjacent points							
2	Int. Critical Tables V3, p 117				mass	tangent with that slope passes through V at that X.							
3					A= H2O	18.0153	Better results possible with more finely spaced data.						
4	ICT data:				B= C2H5OH	46.0690	ICT gives data every 0.1 wt%						
5	w/w	(g/mL)	moles in 100 g:		mL/mole		partial molar volumes						
6	%B	density	nB	nA	nTOT	XB	Vm	slope	water	EtOH	30% tangent		
7	0	0.99823	0.000	5.551	5.551	0.00000	18.0472	36.77	18.0472	54.8124	17.8893		
8	1	0.99636	0.022	5.495	5.517	0.00393	18.1919	36.36	18.0488	54.4087			
9	5	0.98938	0.109	5.273	5.382	0.02017	18.7805	35.69	18.0607	53.7524			
10	10	0.98187	0.217	4.996	5.213	0.04164	19.5377	34.95	18.0824	53.0300			
11	15	0.97514	0.326	4.718	5.044	0.06455	20.3317	34.59	18.0988	52.6888			
12	20	0.96864	0.434	4.441	4.875	0.08906	21.1778	34.78	18.0806	52.8580			
13	25	0.96168	0.543	4.163	4.706	0.11532	22.0972	35.45	18.0089	53.4607			
14	30	0.95382	0.651	3.886	4.537	0.14354	23.1092	36.37	17.8893	54.2555			
15	35	0.94494	0.760	3.608	4.368	0.17394	24.2290	37.28	17.7445	55.0248			
16	40	0.93518	0.868	3.331	4.199	0.20679	25.4673	38.08	17.5934	55.6702			
17	45	0.92472	0.977	3.053	4.030	0.24240	26.8356	38.70	17.4549	56.1548			
18	50	0.91384	1.085	2.775	3.861	0.28112	28.3438	39.43	17.2580	56.6926			
19	60	0.89110	1.302	2.220	3.523	0.36971	31.8562	40.03	17.0568	57.0865			
20	70	0.86786	1.519	1.665	3.185	0.47711	36.1893	40.75	16.7461	57.4981			
21	80	0.84344	1.737	1.110	2.847	0.61001	41.6491	41.30	16.4526	57.7573			
22	85	0.83095	1.845	0.833	2.678	0.68905	44.9434	41.98	16.0148	57.9981			
23	90	0.81797	1.954	0.555	2.509	0.77873	48.7325	42.64	15.5247	58.1680			
24	95	0.80424	2.062	0.278	2.340	0.88138	53.1448	43.41	14.8824	58.2946			
25	99	0.79243	2.149	0.066	2.204	0.97482	57.2450	44.00	14.3552	58.3528			
26	100	0.78934	2.171	0.000	2.171	1.00000	58.3640	44.44	13.9235	58.3640	54.2555		

## Partial molar volumes: EtOH-Water



These two graphs show essentially the same data.  
The ordinate scale in Atkins 7th Ed., Fig 7.1 *exaggerates* this.  
8th Ed. Fig 5.1 --- even more exaggerated.

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## Relationship between partial molar volumes

For a two component system:

$$dV = (\partial V/\partial T)_{p,n_1,n_2} dT + (\partial V/\partial p)_{T,n_1,n_2} dp + (\partial V/\partial n_1)_{p,T,n_2} dn_1 + (\partial V/\partial n_2)_{p,T,n_1} dn_2$$

If (p, T) are constant  $dV = V_1 dn_1 + V_2 dn_2$ .

But  $V = n_1 V_1 + n_2 V_2$

Take differentials:

$$dV = n_1 dV_1 + n_2 dV_2 + V_1 dn_1 + V_2 dn_2$$

Thus  $n_1 dV_1 + n_2 dV_2 = 0$  so  $n_1 dV_1 = -n_2 dV_2$

$V_1$  and  $V_2$  are not independent. The slopes of the  $V_k$  vs. X curves at any point are opposite in sign:

$$X_1 (dV_1/dX_1) = -X_2 (dV_2/dX_1)$$

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## Chemical potential of pure ideal gas (review)

For a pure substance

$$d\mu = dG_m = V_m dp - S_m dT$$

If T is constant, for an ideal gas:

$$\mu = \mu^\circ + RT \ln p$$

where  $\mu^\circ = \mu$  when  $p = p^\circ$   
and  $p^\circ = \text{one (atm or bar)}$ .

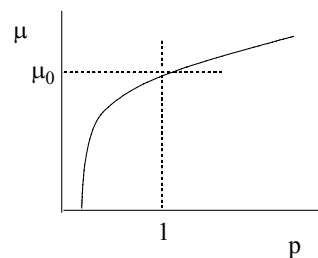
If p falls,  $\mu$  falls.

We used this earlier in discussing condensation:

If  $\mu_{j,\ell} < \mu_{j,g}$  gas molecules j move to liquid: condense.

This lowers  $\mu_{j,g}$  because p falls (by above equation).

Equilibrium vapor pressure is the p at which  $\mu_{j,\ell} = \mu_{j,g}$



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## Mixture of Ideal Gases

For a pure ideal gas at constant T:

$$\mu = \mu^\circ + RT \ln p$$

For a mixture of ideal gases:

$$d\mu_k = V_k dp - S_k dT \quad (\text{derived on slide \#14})$$

but these are now **partial** molar V, S, G.

For ideal gases  $V = n_{\text{tot}} RT/p = (n_1 + n_2 + \dots) RT/p$

So for gas k,  $V_k \equiv (\partial V/\partial n_k)_{p,T,n'} = RT/p$

For an ideal gas,

all partial molar volumes = molar volume!

If T is constant  $d\mu_k = RT dp/p$

so  $\mu_k = \mu_k^\circ + RT \ln (p/p^\circ)$

$$\mu_k = \mu_k^\circ + RT \ln p$$

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## Mixtures of Ideal Gases (2)

Pure ideal gas k:  $\mu_k = \mu_k^\circ + RT \ln p$

Mixture of ideal gases:  $\mu_k = \mu_k^\circ + RT \ln p$

Are these the same? No!

The first  $\mu$  is for **pure** k, the second for k in a **mixture** with some composition. To emphasize this, we can write explicitly what each depends on (and add \* for pure):

Pure ideal gas k:  $\mu_k^*(T, p) = \mu_k^{\circ*}(T) + RT \ln p$

Mixture:  $\mu_k(T, p, X) = \mu_k^\circ(T, X) + RT \ln p$

How does composition X influence  $\mu$ ?

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## How does $\mu$ depend on composition $X_k$ in a mixture of ideal gases?

For pure k (indicated by \*) at pressure  $p = p_k$

$$\mu_k^*(T, p_k) = \mu_k^{\circ*}(T) + RT \ln p_k$$

For a mixture:  $\mu_k(T, p, X) = \mu_k^\circ(T, X) + RT \ln p$

But partial pressure  $p_k = X_k p$ , so  $p = p_k / X_k$

$$\mu_k(T, p, X) = \mu_k^\circ(T, X) + RT \ln (p_k / X_k)$$

$$\mu_k(T, p, X) = \mu_k^\circ(T, X) + RT \ln p_k - RT \ln X_k$$

But ideal gases don't interact:

gas k at a given  $(T, p_k)$  has the same chemical potential whether it is pure or mixed:

$$\mu_k(T, p, X) = \mu_k^*(T, p_k)$$

$$\mu_k^\circ(T, X) + RT \ln p_k - RT \ln X_k = \mu_k^{\circ*}(T) + RT \ln p_k$$

Therefore  $\mu_k^\circ(T, X) = \mu_k^{\circ*}(T) + RT \ln X_k$

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## How $\mu$ depends on composition

From previous slide:

$$\mu_k(T, p, X) = \mu_k^\circ(T, X) + RT \ln p_k - RT \ln X_k$$

$$\mu_k^\circ(T, X) = \mu_k^{\circ*}(T) + RT \ln X_k$$

Substitute:

$$\mu_k(T, p, X) = \mu_k^{\circ*}(T) + RT \ln X_k + RT \ln p_k - RT \ln X_k$$

$$\mu_k(T, p, X) = \mu_k^{\circ*}(T) + RT \ln p_k \quad (1)$$

But  $p_k = X_k p$  so

$$\mu_k(T, p, X) = \mu_k^{\circ*}(T) + RT \ln p + RT \ln X_k \quad (2)$$

At a given  $(p, T)$ , the chemical potential of k is lower in a mixture than in pure k, since  $\ln X < 1$ .

Find another equation for  $\mu_k(T, p, X)$ ...

[Why? you may be asking..]

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## $\mu_k(T, p, X)$ for ideal gas mixtures

$$\mu_k(T, p, X) = \mu_k^{\circ*}(T) + RT \ln p_k \quad (1)$$

$$\mu_k(T, p, X) = \mu_k^{\circ*}(T) + RT \ln p + RT \ln X_k \quad (2)$$

Using  $\mu_k^*(T, p) = \mu_k^{\circ*}(T) + RT \ln p$

$$\mu_k(T, p, X) = \mu_k^*(T, p) + RT \ln X_k \quad (3)$$

Keep in mind: \* means **pure** and  $^\circ$  means **at  $p = p^\circ$**

Which equation we use depends on circumstances.

**Together they tell how the chemical potential of an ideal gas k in a mixture depends on temperature and partial pressure, total pressure, and/or composition.**

A key point is that for ideal gases, the dependence of  $\mu_k$  on  $p$ ,  $p_k$ , and  $X$  has the **same logarithmic form**.

(These equations are used for derivations, not calculations.)

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