# Lecture 17
# Chemistry 163B

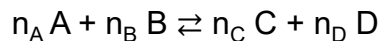$\mu_i$ and $\Delta\mu_{reaction}$

Activity

Equilibrium

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*goals*

- Derive equilibrium and spontaneity criteria applying
  multicomponent thermodynamic relationships;
  i.e. chemical potential ($\Delta\mu_{reaction}$ )

- Define concentration dependence of μ in terms of **activity**
  (fugacity) of 'real' gases, actual solutes

- Apply **activity** to equilibrium $K_{eq}$

- Derive how to obtain fugacity (effective pressure) of **REAL** gas

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*spontaneity and equilibrium in terms of $\Delta\mu$*

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$$n_A\,A + n_B\,B \rightleftarrows n_C\,C + n_D\,D$$

$$\nu_A = -n_A \quad \nu_B = -n_B \quad \nu_C = +n_C \quad \nu_D = +n_D$$

d$\xi$ is extent of reaction
d$\xi$ > 0 forward reaction
d$\xi$ < 0 reverse reaction

$$dn_i = \nu_i\,d\xi$$
$dn_i$ > 0 substance $i$ increases
$dn_i$ < 0 substance $i$ decreases

e.g. $i$ ="products" $\nu_i$ >0 and d$\xi$>0 $\Rightarrow$ $dn_i$ > 0 forward reaction products increase
d$\xi$<0 $\Rightarrow$ $dn_i$ < 0 reverse reaction products decrease

e.g. $i$ ="reactants" $\nu_i$ < 0 and d$\xi$>0 $\Rightarrow$ $dn_i$ < 0 forward reaction reactants decrease
d$\xi$<0 $\Rightarrow$ $dn_i$ > 0 reverse reaction reactants increase

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*equilibrium in terms of $\Delta\mu$*

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$dG_{T,P} < 0$ spontaneous

$dG_{T,P} = 0$ equilibrium

whole pot of mixed reactants and products

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i \qquad \boxed{dn_i = \nu_i d\xi}$$

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i \nu_i\, d\xi$$

$$dG_{T,P} = \left( \sum_{i=1}^{N} \mu_i \nu_i \right) d\xi \leq 0$$

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*equilibrium in terms of $\Delta\mu$*

$$dG_{T,P} = \underbrace{\left( \sum_{i=1}^{N} \mu_i \nu_i \right) d\xi}_{?} \leq 0$$

$$dG_{T,P} = \underbrace{\left( \sum_{i=1}^{N} \mu_i \nu_i \right)}_{\Delta\mu_{reaction}} d\xi \leq 0$$

NOTE: $\mu_i$ IS INTENSIVE (J mol⁻¹)
$\Delta\mu_{reaction}$ IS EXTENSIVE (J)

$$\boxed{dG_{T,P} = \Delta\mu_{reaction} d\xi \leq 0}$$

$\Delta\mu_{reaction} < 0$ forward reaction spontaneous $(d\xi > 0)$

$\Delta\mu_{reaction} > 0$ reverse reaction spontaneous $(d\xi < 0)$

$\Delta\mu_{reaction} = 0$ equilibrium

just like $\Delta$G !!!

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*concentration dependence of $\mu_i$*

**ideal gas, one component (pure substance)**

$$\bar{G} = \bar{G}^{\circ} + RT \ln\left( \frac{P}{1\ bar} \right)$$

**led to**

$$\Delta G_{reaction} = \Delta G_{reaction}^{\circ} + \underline{R}T \ln(Q_P)$$

**what about if other species present?**

$$\mu_i = \mu_i^{\circ} + RT \ln\left( \frac{P_i}{1\ bar} \right)$$

$$\Delta\mu_{reaction} = \Delta\mu_{reaction}^{\circ} + \underline{R}T \ln Q_P$$

**HANDOUT #45**

$$\Delta\mu_{reaction}^{\circ} = \sum_i \nu_i \mu_i^{\circ} \quad Q_P = \prod_i \left( \frac{P_i}{1\ bar} \right)^{\nu_i}$$

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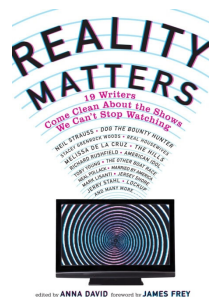*yada -yada- yada: and so forth for $\Delta\mu_{reaction}$*

$$\Delta\mu^{\circ}_{reaction} = -\underline{R}T\,\ln K_P$$

$$\left(\frac{\partial\frac{\Delta\mu}{T}}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \quad where \quad \Delta H = \sum_i v_i\bar{H}_i = \sum_i v_i\left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j\neq n_i}$$

$$\left(\frac{\partial\ln K}{\partial T}\right)_P = \frac{\Delta H^{\circ}}{\underline{R}T^2} \quad where \quad \Delta H^{\circ} = \sum_i v_i\bar{H}^{\circ}_i$$

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*correcting for REALITY (activity and fugacity)*



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*correcting for REALITY (activity and fugacity)*

- will define activity and fugacity coefficients $\gamma_i$'s that provides corrections for the deviation of chemical potential from the **ideal** gas and solute concentration dependence

- activity and fugacity coefficients are obtained from experimental measurements on **REAL** systems or by theory (Debye-Huckel)

> The word fugacity is derived from the Latin fugere, to flee. In the sense of an "escaping tendency", it was introduced to thermodynamics in 1901 by the American chemist Gilbert N. Lewis.
>
> Fugacity - Wikipedia

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*more general $\mu_i$ and corrections for non-ideality (~E&R eqn 9.50, p255)$_{4th}$*

$$\mu_i(T) = \mu_i^{\circ}(T) + RT\, ln\left(\frac{a_i}{a_i^0}\right)$$

standard conditions

how $\mu_i$ 'really' changes in going from standard conditions to actual conditions

$a_i = activity\ of\ component\ i$

$a_i = \gamma_i \times [ideal\ measure\ of\ pressure, concentration, etc]$

$\gamma_i$ is activity coefficient, a correction for non-ideality

$a_i^o = 1\quad unit\quad (bar, molar, etc)$

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*more general $\mu_I$ and corrections for non-ideality*

$$\Delta\mu_{reaction} = \Delta\mu^o + \underline{R}T \ln Q$$

*where now* $Q$ *is written in terms of activities*

$$Q = \prod_i \underbrace{\left(\frac{a_i}{a_i^\circ}\right)^{\bar{v}_i}}_{unitless} \qquad Q = \underbrace{\frac{\left(a_C/a_C^0\right)^{\bar{n}_C} \left(a_D/a_D^0\right)^{\bar{n}_D}}{\left(a_A/a_A^0\right)^{\bar{n}_A} \left(a_B/a_B^0\right)^{\bar{n}_B}}}$$

*sometimes the* $a_i^\circ=1$ *'unit'*
*is omitted but rember Q is 'unitless'*

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*fugacity of gases*

**1. GASES:**

$$a_i = f_i = \gamma_i \, P_i \quad \leftarrow \text{partial pressure}$$

*fugacity of gas*

*fugacity coefficient*

$$Q = \frac{\left(a_C\right)^{\bar{n}_C} \left(a_D\right)^{\bar{n}_D}}{\left(a_A\right)^{\bar{n}_A} \left(a_B\right)^{\bar{n}_B}}$$

$$Q = \frac{\left(\gamma_C \dfrac{P_c}{1bar}\right)^{\bar{n}_C} \left(\gamma_D \dfrac{P_D}{1bar}\right)^{\bar{n}_D}}{\left(\gamma_A \dfrac{P_A}{1bar}\right)^{\bar{n}_A} \left(\gamma_B \dfrac{P_B}{1bar}\right)^{\bar{n}_B}}$$

*correction for non-ideality*

*ideal gas* $Q_P$

$$Q = \left(\frac{\gamma_C^{\bar{n}_C} \gamma_D^{\bar{n}_D}}{\gamma_A^{\bar{n}_A} \gamma_B^{\bar{n}_B}}\right) \frac{\left(\dfrac{P_C}{1bar}\right)^{\bar{n}_C} \left(\dfrac{P_D}{1bar}\right)^{\bar{n}_D}}{\left(\dfrac{P_A}{1bar}\right)^{\bar{n}_A} \left(\dfrac{P_B}{1bar}\right)^{\bar{n}_B}} = \underline{\underline{\gamma}} \, Q_P$$

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*other conventions for activities*

2. pure solids and liquids

$$\mu_i(T,P) \approx \mu_i^\circ(T, P = 1bar)$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i \quad \text{(small for liquid or solid)}$$

*so $a_i \approx 1$ for pure solid or liquid*
*[unless extreme pressure]*

*EXPERT*

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*other conventions for activities*

3. solutes in solutions

$$a_i = \gamma_i \left[I\right]$$

concentration of $I$,
usually molar
but may be $X_i$

WHY CONCENTRATION FOR SOLUTES IN SOLUTION ?
HAVE PROVEN , $P_i = X_i P_{TOTAL} \Rightarrow Q$ FOR IDEAL GAS.
SOON WILL JUSTIFY [I] = $X_i \Rightarrow Q$ FOR , SOLUTES IN IDEAL SOLNS.

activity coefficient $\gamma_i$ corrects 'ideal' measure of 'concentration

if "activity coefficients unity"

$$a_i = \left[I\right] \qquad a_i \equiv f_i = P_i \qquad a_i = 1$$

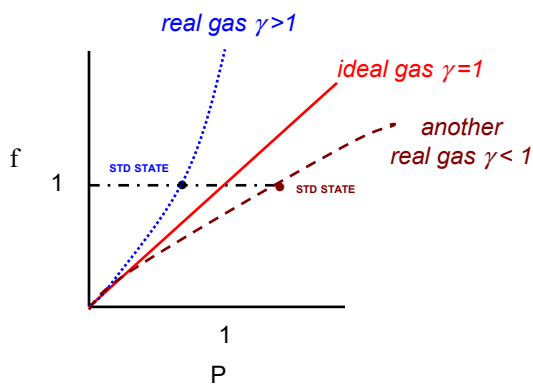*solute*      *gas*        *pure liquid or solid*

HW#7    $\gamma$=1   except prob. 41* and 43.

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*how to evaluate activity (fugacity) coefficients for real gases*
*(HW7 \*#41)*



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*how to evaluate activity (fugacity) coefficients for real gases*

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \bar{V} \quad and$$

$$\mu = \mu^{\circ} + RT \ln f \qquad \boxed{\textit{need in a moment}}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = RT\left(\frac{\partial \ln f}{\partial P}\right)_{T,n}$$

$$so \quad RT\left(\frac{\partial \ln f}{\partial P}\right)_{T,n} = \bar{V}$$

$$\boxed{\text{expression for } d\ln\left(\frac{f}{P}\right) \text{ will prove useful}}$$

$$\left(\frac{\partial \ln\left(\frac{f}{P}\right)}{\partial P}\right)_{T,n} = \left(\frac{\partial(\ln f - \ln P)}{\partial P}\right)_{T,n} = \left(\frac{\partial \ln f}{\partial P}\right)_{T,n} - \left(\frac{\partial \ln P}{\partial P}\right)_{T,n}$$

$$= \frac{1}{RT}\bar{V} - \frac{1}{P} = \frac{1}{RT}\left(\bar{V} - \frac{RT}{P}\right)$$

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**how to evaluate activity (fugacity) coefficients for real gases**

$$\int_{P_1}^{P} d\left( ln\, \frac{f}{P'} \right) = \int_{P_1}^{P} \frac{1}{RT}\left( \bar{V} - \frac{RT}{P'} \right) dP'$$

$$ln\left( \frac{f(P)}{P} \right) - ln\left( \frac{f(P_1)}{P_1} \right) = \frac{1}{RT}\int_{P_1}^{P}\left( \bar{V} - \frac{RT}{P'} \right) dP'$$

$$ln\left( \frac{f(P)}{P} \right) = ln\left( \frac{f(P_1)}{P_1} \right) + \frac{1}{RT}\int_{P_1}^{P}\left( \bar{V} - \frac{RT}{P'} \right) dP'$$

$P_1 \to 0$

$\dfrac{f(P_1)}{P_1} \to 1$

$ln\left( \dfrac{f(P_1)}{P_1} \right) \to 0$

$\left( \bar{V}_{ACTUAL} - \bar{V}_{IDEAL\ GAS} \right)$

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**how to evaluate activity (fugacity) coefficients for real gases**
**(eqn 7.20 E&R$_{4th}$ and HW7 #*41 )**

$$\ln f(P) = \ln P + \frac{1}{RT}\int_{P_1 \to 0}^{P}\left( \bar{V} - \frac{RT}{P'} \right) dP' = \ln P + \frac{1}{RT}\int_{P_1 \to 0}^{P}\left( \bar{V}_{ACTUAL} - \bar{V}_{IDEAL\ GAS} \right) dP'$$

$$\ln\left( \frac{f(P)}{P} \right) = \ln(\gamma) = \frac{1}{RT}\int_{P_1 \to 0}^{P}\left( \bar{V} - \frac{RT}{P'} \right) dP' = \frac{1}{RT}\int_{P_1 \to 0}^{P}\left( \bar{V}_{ACTUAL} - \bar{V}_{IDEAL} \right) dP'$$

$$z = \frac{\bar{V}_{actual}}{\bar{V}_{ideal}} = \frac{P\bar{V}_{actual}}{RT} \quad (compression\ factor\ E\&R_{4th}\ eqn.\ 7.6)$$

$$ln\,\gamma = \frac{1}{RT}\int_{P_1 \to 0}^{P} \bar{V}_{ideal}(z-1)dP' = \int_{P_1 \to 0}^{P} \frac{(z-1)}{P'}dP' \qquad \boxed{HW7\ 41^*}$$

$$\gamma(P,T) = exp\left[ \int_{P_1 \to 0}^{P} \frac{z-1}{P'}dP' \right] \quad (E\&R_{4th}\ eqn\ 7.21)$$

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*goals*

👆 • Derive equilibrium and spontaneity criteria applying

multicomponent thermodynamic relationships;

i.e. chemical potential ($\Delta\mu_{reaction}$ )

👆 • Define concentration dependence of $\mu$ in terms of **activity**

(fugacity) of 'real' gases, actual solutes

👆 • Apply **activity** to equilibrium $K_{eq}$

👆 • Derive how to obtain fugacity (effective pressure) of **REAL** gas

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*End of Lecture 17*

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*activity for solids and liquids  ($P_{total} \neq$ 1 bar)*

$$\mu_i(T) = \mu_i^{\circ}(T) + RT \, ln\left( \frac{a_i}{a_i^0} \right)$$

$$\left( \frac{a_i}{a_i^0} \right) = e^{\frac{\mu_i(T) - \mu_i^{\circ}(T)}{RT}}$$

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T,n} = \bar{V}_i$$

$$\mu_i(T, P_{total}) = \mu_i^o(T, 1 \text{ bar}) + \int_{1bar}^{P_{total}} \bar{V}_i dP \approx \mu_i^o(T, 1 \text{ bar}) + \bar{V}_i(P_{total} - 1 \text{ bar}) \quad \boxed{\text{HW\#6  37 (E\&R}_{4th}\text{ 6.42)}}$$

$$\left( \frac{a_i}{a_i^0} \right)_{l \text{ or } s} \approx e^{\frac{\bar{V}_i(P_{total} - 1 \text{ bar})}{RT}} \approx 1 \text{ for } P_{total} \text{ near 1 bar (since } \bar{V} \text{ is small for liquids or solids)}$$

for $\Delta\mu$ at high $P_{total}$
would use this in Q
for liquids and solids

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*Midterm #2,  Friday  28th  February*

• Exam WILL COVER material on lectures #8-#15 *(#1-#15)*
(~through Wednesday , 19th  February)  and HW#4-HW#6

• Weeks 4-6+ "reviews" on WWW handouts (19th February)

• HW solutions on CANVAS (HW#6 Fri, 21st February)

• SAMPLE  ('~~practice~~') midterm on CANVAS reserve
Saturday, 22nd   February
*(see sample exam for 'relationships provided')*

• TAs have KEY for use in sections, tutorials, and office hours
(on  CANVAS ~25th February)

• REVIEW SESSION
Wednesday, 26th February, Classroom Unit 2, 7:00-8:00 PM

• Midterm #2 Exam, Friday 28th February
done "in place"
no ear dingies (iPODs, MP3, etc)
bring charged calculators
get here ON TIME

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