# Lecture 17
Chemistry 163B

μ_i and $\Delta\mu_{reaction}$

Activity

Equilibrium

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

$$n_A A + n_B B \rightleftarrows n_C C + n_D D$$
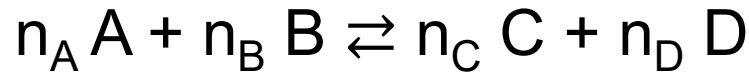
$$\nu_A = -n_A \quad \nu_B = -n_B \quad \nu_C = +n_C \quad \nu_D = +n_D$$

$d\xi$ 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

$dG_{T,P} < 0$ spontaneous

$dG_{T,P} = 0$ equilibium

whole pot of mixed reactants and products

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

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

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

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: μ_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 ΔG !!!

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concentration dependence of μ_i

ideal gas, one component (pure substance)

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

led to

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

what about if other species present?

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

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

$$\Delta\mu^{\circ}_{reaction} = \sum_i \nu_i \mu_i^{\circ} \qquad Q_P = \prod_i \left(\frac{P_i}{1\,bar}\right)^{\nu_i}$$
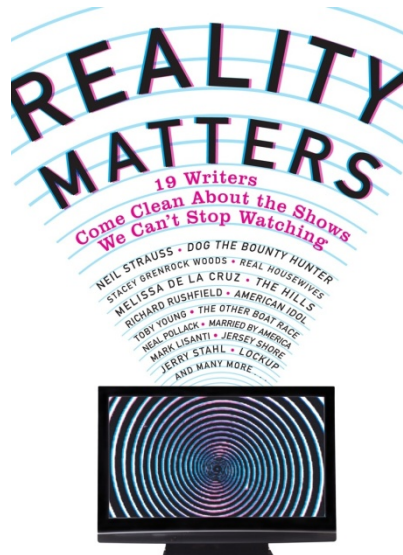
HANDOUT #45

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

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

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

- will define activity and fugacity coefficients γ_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

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

standard
conditions

how μ_i 'really' changes
in going from standard
conditions to actual conditions

$$a_i = activity \; of \; component \; i$$

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

γ_i is activity coefficient, a correction for non-ideality

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

$$\Delta\mu_{reaction} = \Delta\mu^o + \underline{R}T \; lnQ$$

where now Q is written in terms of activities

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

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

1. GASES:

$$a_i = f_i = \gamma_i\, P_i$$

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

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

other conventions for activities

2. pure solids and liquids

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

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

so $a_i \approx 1$ for pure solid or liquid

[unless extreme pressure]

EXPERT

other conventions for activities

3. solutes in solutions

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.

$$a_i = \gamma_i [I]$$

activity coefficient γ_i corrects 'ideal' measure of 'concentration

if "activity coefficients unity"
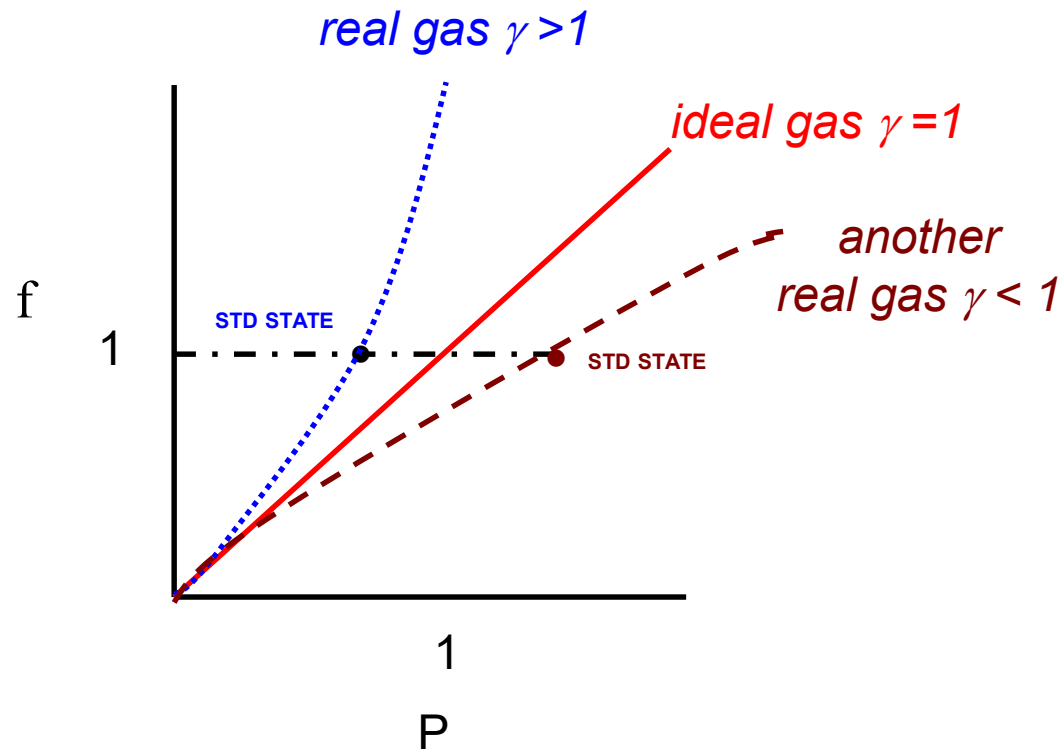
$$a_i = [I] \qquad a_i \equiv f_i = P_i \qquad a_i = 1$$

solute   *gas*   *pure liquid or solid*

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

real gas $\gamma > 1$

ideal gas $\gamma = 1$

another real gas $\gamma < 1$

f

STD STATE

1

STD STATE

1

P

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how to evaluate activity (fugacity) coefficients for real gases

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

$$\mu = \mu^{\circ} + RT \ln f$$

need in a moment

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

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

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

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

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

how to evaluate activity (fugacity) coefficients for real gases

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

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

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

$$P_1 \rightarrow 0$$

$$\frac{f(P_1)}{P_1} \rightarrow 1$$

$$ln\left(\frac{f(P_1)}{P_1}\right) \rightarrow 0$$

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

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

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

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

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

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

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

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End of Lecture 17

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

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

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

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

$$\mu_i(T, P_{total}) = \mu_i^o(T, 1 \text{ bar}) + \int_{1bar}^{P_{total}} \overline{V}_i dP \approx \mu_i^o(T, 1 \text{ bar}) + \overline{V}_i\left(P_{total} - 1 \text{ bar}\right)$$

HW#6 37 (E&R$_{4th}$ 6.42)

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

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

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- 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