Lecture 17
Chemistry 163B

μ_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 Δμ

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

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

dξ is extent of reaction
dξ > 0 forward reaction
dξ < 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 Δμ

$dG_{T,P} < 0$ spontaneous

$dG_{T,P} = 0$ equilibium

whole pot of mixed reactants and products

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

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

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

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equilibrium in terms of Δμ

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

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

NOTE: μ_i IS INTENSIVE (J mol^{-1})
$\Delta\mu_{reaction}$ IS EXTENSIVE (J)

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

$\Delta\mu_{reaction} < 0$ 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)

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

led to

$$\Delta G_{reaction} = \Delta G^{\circ}_{reaction} + RT\, ln(Q_P)$$

what about if other species present?

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

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

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

HANDOUT #45

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

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

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

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

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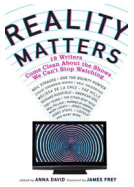
correcting for REALITY (activity and fugacity)



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correcting for REALITY (activity and fugacity)

- will define activity and fugacity coefficients **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

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

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

standard conditions

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

a_i = *activity of component i*

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

γ_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 μ_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

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

sometimes the a_i^0=1 'unit' is omitted but rember Q is 'unitless'

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fugacity of gases

1. GASES:

$a_i = f_i = \gamma_i P_i$ ← partial pressure

fugacity of gas

fugacity coefficient

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

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

correction for non-ideality

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

ideal gas Q_P

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other conventions for activities

2. pure solids and liquids

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

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

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

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other conventions for activities

3. solutes in solutions

$$a_i = \gamma_i [I]$$

concentration of I, usually molar but may be X_i

WHY CONCENTRATION FOR SOLUTES IN SOLUTION ? HAVE PROVEN $P_i = X_i P_{i\,PURE}$ ➡ 0 FOR IDEAL GAS. SOON WILL JUSTIFY $[I] = X_i$ ➡ 0 FOR SOLUTES IN IDEAL SOLNS.

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 γ=1 except prob. 41* and 43.

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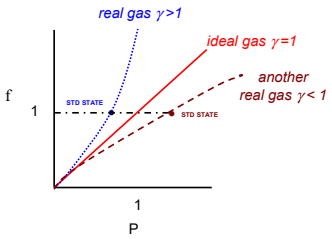
*how to evaluate activity (fugacity) coefficients for real gases (HW7 *#41)*



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how to evaluate activity (fugacity) coefficients for real gases

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

$$\mu = \mu^* + RT \ln f$$

need in a moment

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

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

expression for $d\ln\left(\frac{f}{P}\right)$ 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

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

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

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

$P_i \to 0$

$\frac{f(P_i)}{P_i} \to 1$

$\ln\left(\frac{f(P_i)}{P_i}\right) \to 0$

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

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

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

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

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

$$\ln\gamma = \frac{1}{RT}\int_{P_i \to 0}^{P} \bar{V}_{ideal}(z-1)dP' = \int_{P_i \to 0}^{P} \frac{(z-1)}{P'} dP'$$

HW7 41*

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

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End of Lecture 17

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

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

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

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

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

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

$$\left(a_i / a_i^0\right)_{l\text{ or }s} = e^{\frac{\bar{V}_i(P_{total} - 1\text{ bar})}{RT}} = 1$$ **for P_{total} near 1 bar (since $\bar{V}$ 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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