3.020 Lecture 18

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1 Estimating properties of reacting gas systems

Consider reaction $\mathrm{A} + \mathrm{B} \longleftrightarrow 2\,\mathrm{C}$
Q. What can we learn from plots of free energy v.s. composition ?

$$G' = \sum_i n_i \mu_i = \sum_i n_i \mu_i^0 + \sum_i n_i RT \ln (P_i/P)$$

n_i : composition
μ_i^0 : chem. potential at pure component i at pressure P
RT, $\ln (P_i/P)$: system at fixed T and P

- Univariant reacting system $\longrightarrow$ composition can be expressed in terms of a single variable
  - wirte w.r.t. n_c

$$dn_A = dn_B = -\frac{1}{2} dn_c$$
$$n_A = n_{A,i} + \int dn_A = n_{A,i} - \frac{1}{2}(n_C - n_{C,i})$$
$$n_B = n_{B,i} + \int dn_B = n_{B,i} - \frac{1}{2}(n_C - n_{C,i})$$
$$n_c = n_c$$

constant for this particular rx'n, not so in general

  - also need $n_{TOT} = n_A + n_B + n_C = n_{A,i} + n_{B,i} + n_{C,i}$ to write $P_i = P \frac{n_i}{n_{TOT}}$

- now can write out $G'(n_C)$ and plot

$$G' = (n_{A,i} - \frac{1}{2}(n_C - n_{C,i}))\,\mu_A^0 + (n_{B,i} - \frac{1}{2}(n_C - n_{C,i}))\,\mu_B^0 + n_C\,\mu_C^0 + \sum_i RT n_i \ln (\frac{n_i}{n_{TOT}})$$

- consider $H_2 + Cl_2 \longleftrightarrow 2\,HCl$ at 298 K

$$\mu^0_{H_2} = \underbrace{H^0_{H_2}}_{0} - TS^0_{H_2} \quad \longleftarrow \quad \textbf{by definition, enthalpy convention of elements}$$

$$\mu^0_{Cl_2} = \underbrace{H^0_{Cl_2}}_{0} - TS^0_{Cl_2} \quad \longleftarrow \quad \textbf{in their standard state at 298K, 1 atm is set to zero}$$

$$\mu^0_{HCl} = \underbrace{H^0_{HCl}} - TS^0_{HCl}$$

this is the formation enthalpy for 1 mole of HCl from the elements

$\frac{1}{2}\,H_2 + \frac{1}{2}\,Cl \overset{\Delta_f\,H}{\longleftrightarrow} HCl$

Q1) Le Chatelier says that reacting systems "resist" temp. rises by running in endothermic direction
this rxn. is observed to run to <u>left</u> with increasing T, so as written it is <u>exothermic</u>

- van't Hoff says $\frac{d\ln K_P}{dT} = \frac{\Delta H^0}{RT^2}$

Q2) Using van't Hoff, if we can estimate $\frac{d\ln K_p}{dT}$, then we can estimate ΔH^0

temp	n_C @ equil	$n_A = n_B$ @ equil	K_P
298K	1.55	0.225	47.5
328K	1.53	0.235	42.5

- using these estimates

$$\Delta \ln K_P = -0.114$$

$$\Delta T = 30K \quad \Longrightarrow \frac{d\ln K_P}{dT} \approx -0.00379K^{-1}$$

$$\Delta H^0 = RT^2 \frac{d\ln K_P}{dT} \approx -3.09\ kJ$$

T : use midpoint temp, 313 K; exothermic

Challenge 1: How do we find temp-dependence of μ^0_i's?
Challenge 2: Can we estimate ΔC_P from a temperature series of $G'(n_C)$ data?

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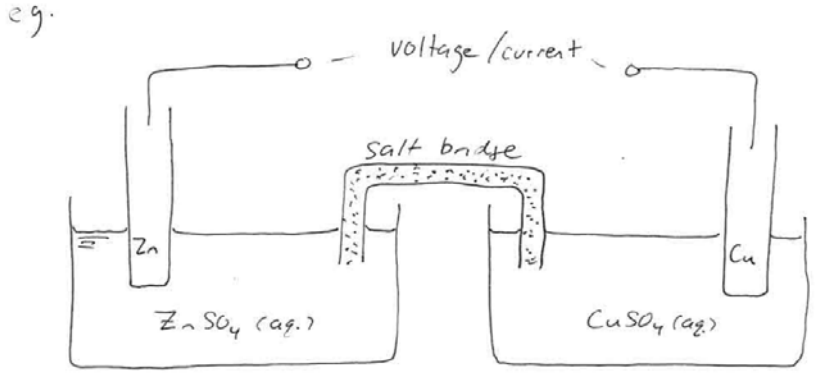
2 Nernst in a nutshell

- Take a redox reaction
  e.g. $\mathrm{Zn} + \mathrm{CuSO_4} \longleftrightarrow \mathrm{ZnSO_4} + \mathrm{Cu}$
- Separate reduction & oxidation half-reactions in a device engineered such that electrons and ions follow separate paths



- Electrostatic work of moving charge nF across potential $\mathscr{E}$:

$$-W^* = -\Delta U = \int d\underline{x} \cdot \underline{E} nF = nF\mathscr{E}$$

- n is the moles of fundamental charge, and $F = 96485$ C/mole is Faraday's constant
- $\mathscr{E}$ = electro-motive force (EMF) = potential difference across the cell
- Generalized work theorem

$$\Delta G = W^* \quad \longleftarrow \quad \textbf{reversible, non-mechanical work}$$

Nernst equation : $\Delta G = -nF\mathscr{E}$

- Use formalism of reacting systems to write ΔG w.r.t. activities/ concentrations

$$\textbf{e.g.} \quad \Delta G = \Delta G^0 + RT \ln \underbrace{\left(\frac{a_{ZnSO_4}\ a_{Cu}}{a_{CuSO_4}\ a_{Zn}}\right)}_{\textbf{reaction quotient Q}}$$

- Use Nernst to couple electrostatics to chemistry

$$nF \underbrace{\mathscr{E}}_{\textbf{cell voltage}} = - \underbrace{\Delta G^0}_{\textbf{reference}} - RT \ln \underbrace{Q}_{\textbf{concentrations}}$$

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e.g. for Daniell cell, we have

$$\mathscr{E} = \mathscr{E}^0 - \frac{RT}{2F} \ln \frac{[ZnSO_4]}{[CuSO_4]}$$

$[x]$ = concentration in aqueous solution
$\mathscr{E}^0$ = reference potential for $[ZnSO_4] = [CuSO_4] = 1m$
$n = 2$ because redox reaction involves 2 electrons

3.020 Thermodynamics of Materials

Spring 2021