3.020 Lecture 14

Prof. Rafael Jaramillo

1 Gas phase reaction at equilibrium at fixed T & P

$$\text{reaction A} + \text{B} = 2\,\text{C}$$

$$dG^{'} = -S^{'}\underbrace{dT}_{0} + V^{'}\underbrace{dP}_{0} + \sum_i \mu_i dn_i$$

Equilibrium determined by :

- chemical potentials μ_i
- mole #s dn_i

- At equilibrium $dG^{'} = \sum_i \mu_i dn_i = 0$

Q. How many independent variables ?

Reaction balance means there's only 1 degree of freedom

from L/O

e.g. reaction extent $d\xi$

- Apply constraints, here using n_c as independent variable

$$dn_A = \frac{v_A}{v_C}dn_C = -\frac{1}{2}dn_C, \quad dn_B = \frac{v_B}{v_C}dn_C = -\frac{1}{2}dn_C$$

$$dG^{'} = \underbrace{(\mu_A\frac{v_A}{v_C} + \mu_B\frac{v_B}{v_C} + \mu_C)}_{\textbf{coefficient must be 0 @ equilibrium}} \times \underbrace{dn_C}_{\textbf{unconstrained internal variable}} = 0$$

- Substitute ideal gas mixture expression for $\mu_i^{'}$s

$$\begin{aligned} dG^{'} &= [(\mu_A^0 + RT\ln(\frac{P_A}{P_0}))\ \frac{V_A}{V_C} \\ &\quad + (\mu_B^0 + RT\ln(\frac{P_B}{P_0}))\ \frac{V_B}{V_C} \\ &\quad + (\mu_C^0 + RT\ln(\frac{P_C}{P_0}))]\ dn_C \qquad = 0 \end{aligned}$$

μ_i^0 = reference chem. potential for gas i at partial pressure P_0 and temp. T

- Collect like terms and multiply through by V_C

$$(V_A\mu_A^0 + V_B\mu_B^0 + V_C\mu_C^0) + RT\ln(\frac{P_A}{P_0})^{V_A}(\frac{P_B}{P_0})^{V_B}(\frac{P_C}{P_0})^{V_C} = 0$$

- Define $\underbrace{\Delta G^0}\quad = \sum_i v_i\mu_i^0 = 2\mu_C^0 - \mu_A^0 - \mu_B^0$

  free energy change of reaction when all components are in their standard state

---

- Define equilibrium constant $K_P = \prod_i(\frac{P_i}{P_0})^{V_i}$
- Simplify by assuming that total pressure $P = P_0$, so that :

$$P_i/P_0 = X_i$$

$$K_P = \prod_i X_i^{V_i} = \frac{X_C^2}{X_A X_B}$$

- Collect terms to write concise expression for reaction equilibrium condition:

$$\ln K_P = -\frac{\Delta G^0}{RT}, \quad \textbf{or} \quad K_P = e^{-\frac{\Delta G^0}{RT}}$$

Notes on reaction equilibrium

- Negative ΔG^0 drives reaction to the <u>right</u>
- Adding more at a given component shifts reaction balance to maintain equilibrium $\longrightarrow$ <u>Le Chatelier principle</u>
- Any change in the status $qv0$ prompts an opposing reaction in the responding system

---

2 Temperature dependence of reaction equilibrium

$$\frac{\partial}{\partial T}\bigg|_P \ln K_P = \frac{\partial}{\partial T}\bigg|_P \left(-\frac{\Delta G^0}{RT}\right) = \frac{\Delta H^0}{RT^2} - \frac{1}{RT}\frac{\partial \Delta H^0}{\partial T}\bigg|_P + \frac{1}{R}\frac{\Delta S^0}{\partial T}\bigg|_P$$

$$\frac{\partial \Delta H^0}{\partial T}\bigg|_P = \Delta C_P, \quad \frac{\partial \Delta S^0}{\partial T}\bigg|_P = \frac{\Delta C_P}{T} \quad \text{– \textbf{show this}}$$

$$\frac{\partial \ln K_P}{\partial T} = \frac{\Delta H^0}{RT^2} \qquad \text{\textbf{van't Hoff equation}}$$

---

ex. endothermic reaction $Q > 0$

$$\Delta H = Q_{rev}$$

$$\Delta H > 0 \quad \longrightarrow \quad \frac{\partial \ln K_P}{\partial T}\bigg|_P > 0$$

- reax. moves to the right (K_P increases) with increasing temperature
- system "tries" to oppose temperature rise taking up heat in endothermic reaction

Le Chatelier !!