

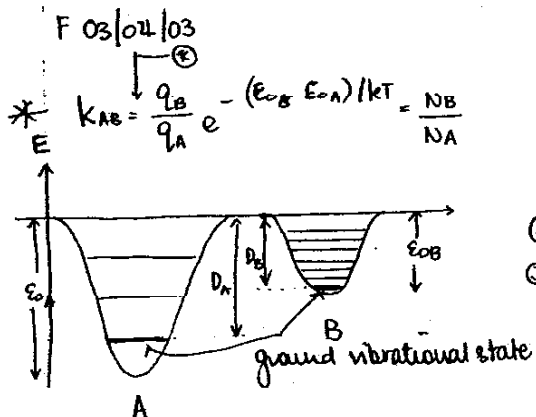
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Course 565/665 Lecture Number _____ Date 4/4/03

Lecturer Dr. Silvia Cavagnero Note Taker Lena Ho



$Q \approx 1(T_{00})$
 $Q \approx 1(T_0)$

Distribution of particles energies is much more exponential when energy levels are far apart or temperatures are low.

$\Delta D = E_{0B} - E_{0A} = D_B - D_A$: can get this from experiments that measure difference in dissociation energies

* Pressure-Based Equilibrium Constants

(it is easier to use p instead of N experimentally to find equilibrium constants)

For a reaction : $aA + bB \rightleftharpoons cC$

Recall for Ideal Gas : $N = \frac{pV}{kT}$

$$K = \frac{N_c^c}{N_A^a N_B^b} = \frac{(p_c V/kT)^c}{(p_A V/kT)^a (p_B V/kT)^b}$$

V and T are constant here

from $\textcircled{*}$
$$= \frac{q_c^c}{q_A^a q_B^b} e^{-\Delta D/kT}$$

Multiply both sides by $(\frac{V}{kT})^{a+b-c}$

$$K_p = \frac{p_c^c}{p_A^a p_B^b} = (kT)^{-(a+b-c)} \frac{q_c^c}{q_A^a q_B^b} e^{-\Delta D/kT}$$

(Defined $q_0 = \frac{q}{V}$) we saw : $\mu = -kT \ln \frac{q'}{N} = -kT \ln \left(\frac{q_0 V}{N} \right) = -kT \ln \left(\frac{q_0 kT}{p} \right)$

Define $p_0 \equiv q_0' kT$; $\mu_0 \equiv -kT \ln p_0$ ← not dimensionless

$$\mu = kT \ln \frac{p}{p_0} = \mu_0 + kT \ln p$$

μ_0 = Chemical potential standard state (function of temperature)

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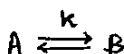
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Course SGS/605 Lecture Number _____ Date 4/4/03

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Skip Le Châtelier's Principle

* Temperature-Dependence of the Equilibrium Constant: Van't Hoff Equation
A derivation:



at equilibrium: $\mu_A = \mu_B$

$$\mu_A^\circ + RT \ln P_A = \mu_B^\circ + RT \ln P_B$$

$$K_p = \frac{P_B}{P_A}$$

$$\ln \frac{P_B}{P_A} = -\frac{(\mu_B^\circ - \mu_A^\circ)}{RT} = -\frac{\Delta \mu^\circ}{RT}$$

$$\Delta \mu^\circ = -RT \ln K_p$$

Can predict K_p with knowledge of μ° and T

$$\Delta \mu^\circ = \Delta H^\circ + T \Delta S^\circ$$

$$\Delta \mu^\circ \cdot N = -NRT \ln K_p$$

$$\Delta G = -RT \ln K_p$$

Valid at constant pressure.

$$\Delta \mu^\circ = \Delta H_N^\circ - T \Delta S_N^\circ \leftarrow \text{per molecule.}$$

$$\left(\frac{\partial \ln K_p}{\partial T} \right)_P = \frac{\partial}{\partial T} \left(\frac{\Delta \mu^\circ}{RT} \right) = -\frac{\partial}{\partial T} (\Delta H_N^\circ - T \Delta S_N^\circ)_P$$

Assuming ΔH° and ΔS° not to be temperature dependent,

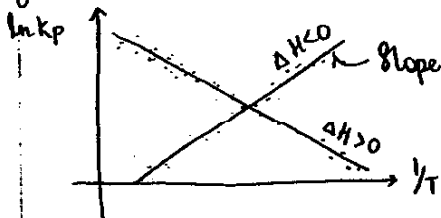
$$\left(\frac{\partial \ln K_p}{\partial T} \right)_P = \left(\frac{\Delta H_N^\circ}{RT^2} \right) = \frac{\Delta H^\circ}{RT^2}$$

This assumption will only be justified if points obtained actually fit a straight line. If they don't, then this assumption is probably not valid.

$$d\left(\frac{1}{T}\right) = -\frac{1}{T^2} dT$$

$$\left(\frac{\partial \ln K_p}{\partial (1/T)} \right)_P = -\frac{\Delta H^\circ}{R}$$

Van't Hoff eqn.



Slope = $-\frac{\Delta H^\circ}{R} \Rightarrow$ determine ΔH°

$\Delta H < 0$: Exothermic

$\Delta H > 0$: Endothermic

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* The Gibbs-Helmholtz Equation

→ Skip demonstration in the book

$$\frac{\partial G/T}{\partial T} = -\frac{H}{T^2}$$

- Assumes H and S are temperature independent
 - Since $\Delta G = \Delta G^\circ + RT \ln K_p$

$$G = H - TS$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P \dots (1)$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2}$$

$$= -\frac{1}{T^2}\left(G - T\left(\frac{\partial G}{\partial T}\right)_P\right)$$

Go back to (1) $\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$ } Gibbs Helmholtz

* What happens if H and S are T-dependent?

$$G(T) = H(T) - TS(T)$$

H) $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ (Biologically relevant)
 $\int_{T_R}^T C_p dT = \int_{H_R}^H dH = H_T - H_R = C_p(T - T_R)$
reference temperature constant p
 C_p is not temperature-dependent

S) $dS = \frac{dQ}{T} = \frac{dH}{T} \Rightarrow C_p = \left(\frac{T \partial S}{\partial T}\right)_P \Rightarrow \frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_P$

$$C_p \int_{T_R}^T \frac{dT}{T} = \int_{S_R}^S dS \Rightarrow S_T - S_{T_R} = C_p \ln \frac{T}{T_R}$$

$$G = H(T) - TS(T) = C_p(T - T_R) + H_R - T[C_p \ln \frac{T}{T_R} + S_{T_R}] = G$$