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Course 565/665 Lecturer Prof. Cavagnero

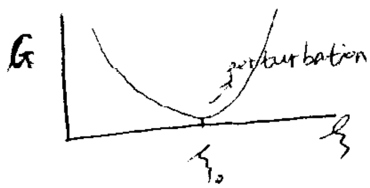
Day 4.9.04 Date 9:55 am

Notes Taken By J. Hong Total Number of Pages

$A \rightleftharpoons B$

$N_B = N\xi \qquad \xi = \frac{N_B}{N} = \frac{N_B}{N_A + N_B}$; in the beginning of rxn. $\xi = 0$

at equilibrium: $\xi_0 = \frac{N_B}{N}$



Towards equilibrium. $dG = (\mu_B - \mu_A) N d\xi < 0$

at constant p, how does K depend on T?

$A \rightleftharpoons B$ at equilibrium. $\mu_A = \mu_B$

$$\mu_A^\circ + kT \ln p_A = \mu_B^\circ + kT \ln p_B$$

$$\ln K_p = \ln \frac{p_B}{p_A} = \frac{-(\mu_B^\circ - \mu_A^\circ)}{kT} = -\frac{\Delta\mu^\circ}{kT}$$

$\Delta\mu^\circ = -kT \ln K_p \qquad \Delta\mu^\circ = \Delta H_{N_0}^\circ - T\Delta S_{N_0}^\circ$ (?)

$\Delta H_{N_0}^\circ \equiv \frac{\Delta H^\circ}{N_0} \qquad \Delta S_{N_0}^\circ \equiv \frac{\Delta S^\circ}{N_0}$

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = -\frac{\partial}{\partial T}\left(\frac{\Delta\mu^\circ}{kT}\right)_p = -\frac{\partial}{\partial T}\left[\frac{\Delta H_{N_0}^\circ - T\Delta S_{N_0}^\circ}{kT}\right]_p$$

If $\Delta H_{N_0}^\circ$, $\Delta S_{N_0}^\circ$ do not depend on T:

write on this side only - do not double side for genchem office

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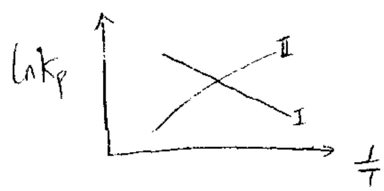
$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H^\circ_{N_0}}{kT^2} = \frac{\Delta H^\circ}{RT^2}$$

Recall: ① $R = N_0 k$ ② $d\left(\frac{1}{T}\right) = -\frac{1}{T^2}dT$

$$\left(\frac{\partial \ln K_p}{\partial \frac{1}{T}}\right)_p = \frac{-\Delta H^\circ_{N_0}}{k} = -\frac{\Delta H^\circ}{R}$$

Van't Hoff equation



2 different situations:

I. $H_B^\circ > H_A^\circ \Rightarrow \Delta H^\circ > 0$ endothermic

II. $H_B^\circ < H_A^\circ \Rightarrow \Delta H^\circ < 0$ exothermic

recall $H = q \Rightarrow$ intrinsic heat or energy (?)

Van't Hoff plot is linear for a lot of small molecule chem rxn.

(ex). know K_p at T_1, calculate K_p at T_2.

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

$$\int_{\ln K_{p(T_1)}}^{\ln K_{p(T_2)}} \ln K_p = -\int_{\frac{1}{T_1}}^{\frac{1}{T_2}} \frac{\Delta H^\circ}{R} d\left(\frac{1}{T}\right)$$

$$\ln K_{p(T_2)} - \ln K_{p(T_1)} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$