T Dependence of Equilibrium Constant

- **Basic issue**
  - we know K_p (or K_c, K_f), for a given reaction expression, is function of temperature only
  - can we describe/model the temperature dependence (for P.G.)
- **Approach**
  - employ previously derived expressions relating Gibbs Free Energy and Enthalpy (van't Hoff)

$$\left.\frac{\partial(G/T)}{\partial T}\right|_{p,n_i} = \frac{-H}{T^2} \quad \text{and for P.G.} \quad \frac{d\left(\mu_i^o/T\right)}{dT} = \frac{-\bar{h}_i}{T^2} = \frac{-\hat{h}_i}{T^2}$$

van't Hoff's Equation

- Start with K_p "definition" (P.G.)

$$\ln K_p = \frac{-1}{\bar{R}T}\sum_i \nu_i \mu_i^o = \frac{-1}{\bar{R}}\sum_i \nu_i \frac{\mu_i^o}{T}$$

- Get T dep. from derivative

$$\frac{d}{dT}\left(\ln K_p\right) = \frac{d}{dT}\left(\frac{-1}{\bar{R}}\sum_i \nu_i \frac{\mu_i^o}{T}\right) = \frac{-1}{\bar{R}}\sum_i \nu_i \underbrace{\frac{d}{dT}\left(\frac{\mu_i^o}{T}\right)}$$

$$= \frac{1}{\bar{R}}\sum_i \nu_i \frac{\hat{h}_i}{T^2}$$

$$\sum_i \nu_i \hat{h}_i = ?$$

$$= \hat{H}^o_{RHS} - \hat{H}^o_{LHS} \equiv \Delta\hat{H}^o_R$$ ***Standard Heat of Reaction***

$$\Delta\hat{H}_R \begin{cases} <0 & \textit{Exothermic} \\ >0 & \textit{Endothermic} \end{cases}$$

$$\boxed{\frac{d\ln K_p}{dT} = \frac{\Delta\hat{H}_R(T)}{\bar{R}T^2}}$$ ***van't Hoff's Eq'n.***

drop ^{o} since P.G. $H \neq H(p)$

K_p Temperature Dependence

- So what is T dependence of K_p

$$\frac{d}{dT}\left(\ln K_p\right)=\frac{\Delta\hat{H}_R(T)}{\bar{R}T^2}\begin{cases}<0 & exothermic\\ >0 & endothermic\end{cases}$$

- From K_p def'n. $$K_p=\frac{\chi_{RHS}^{|\nu_i|}}{\chi_{LHS}^{|\nu_i|}}p^{\Delta n_R} \qquad \Delta n_R\equiv\sum_i \nu_i$$
  - for exothermic reaction: $T\uparrow \Rightarrow K_p\downarrow$ (more LHS)
  - for endothermic reaction: $T\uparrow \Rightarrow K_p\uparrow$ (more RHS)
- Recall p dependence
  - $p\uparrow \Rightarrow$ more lower moles side

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K_c Temperature Dependence

- For P.G., we had

$$\ln K_c=\ln K_p-\ln\left(\bar{R}T\right)^{\sum\nu_i}=\ln K_p-\Delta n_R\ln\left(\bar{R}T\right)$$

$$\frac{d}{dT}\ln K_c=\frac{d}{dT}\ln K_p-\Delta n_R\frac{d}{dT}\ln\left(\bar{R}T\right)=\frac{\Delta\hat{H}_R}{\bar{R}T^2}-\Delta n_R\frac{1}{T}$$

$$=\frac{\Delta\hat{H}_R-\Delta n_R\bar{R}T}{\bar{R}T^2}$$

$$pV=n\bar{R}T \underset{fixed\ T}{\Rightarrow} \Delta(pV)=(\Delta n)\bar{R}T$$

$$=\frac{\Delta\hat{H}_R-\Delta pV}{\bar{R}T^2}$$

$$\boxed{\frac{d}{dT}\ln K_c=\frac{\Delta\hat{U}_R}{\bar{R}T^2}}$$

K_f Temperature Dependence

- Using similar approach for imperfect gases

$$\frac{d}{dT}\ln K_f = \frac{\sum \nu_i \hat{h}_i^o}{\bar{R}T^2}$$

- Pick f^o condition at low enough p such that $f^o/p^o = 1$
  - we can choose any ref. (^{o}) condition we want
  - by choosing low pressure ⇒ PG and $\bar{h}_i = \hat{h}_i$ and since K_f not function of f

$$\frac{d}{dT}\ln K_f = \frac{\Delta H_R^o}{\bar{R}T^2}$$

Interpolating for K_p

$$\frac{d\ln K_p}{dT} = \frac{\Delta\hat{H}_R(T)}{\bar{R}T^2} \Rightarrow \int_{K_{p_1}}^{K_{p_2}} d\ln K_p = \ln\left(K_{p_2}/K_{p_1}\right) = \int_{T_1}^{T_2} \frac{\Delta\hat{H}_R(T)}{\bar{R}T^2}dT$$

- Can usually find information on ΔH_R

$$\Delta\hat{H}_R = \sum \nu_i \hat{h}_i = \sum \nu_i\left(\hat{h}_{i,0} + \int_0^T \hat{c}_{p_i} dT\right) \cong \Delta\hat{H}_{R,0} + \sum \nu_i \int_0^T \left(a_i + b_i T + c_i T^2\right)dT$$

$$\cong \Delta\hat{H}_{R,0} + \sum \nu_i\left(a_i T + \frac{1}{2}b_i T^2 + \frac{1}{3}c_i T^3\right)$$

- For "small" ΔT, assume ΔH_R~constant

$$\ln\frac{K_{p_2}}{K_{p_1}} \approx \frac{\Delta\hat{H}_R(T_1)}{\bar{R}}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

i.e., 2nd term changes slowly works best for strongly exo. or endo. rxns.

- Otherwise

$$\ln K_p \cong C + \frac{1}{\bar{R}}\left\{\frac{-\Delta\hat{H}_{R,T_o}}{T} + \sum \nu_i\left(a_i \ln T + b_i T/2 + c_i T^2/6\right)\right\}$$