T Dependence of Equilibrium Constant

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

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

van't Hoff 1

van't Hoff's Equation

- Start with K_p "definition" (TPG)

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

- Get T dependence 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***

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

drop ^{o} since TPG $H \neq H(p)$

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

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K_p Temperature Dependence

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

- Integrating gives $K_p(T)$ from H data, but 1st, how to interpret this expression?
- From K_p def'n. $\quad K_p=\dfrac{\prod_i \chi_{i,RHS}^{|\nu_i|}}{\prod_i \chi_{i,LHS}^{|\nu_i|}}\,p^{\Delta n_R} \qquad \Delta n_R\equiv\sum_i \nu_i$
  - for exothermic expression: $T\uparrow\Rightarrow K_p\downarrow$ (more LHS)
  - for endothermic expression: $T\uparrow\Rightarrow K_p\uparrow$ (more RHS)
- Recall p dependence
  - $p\uparrow\Rightarrow$ more lower moles side

Interpolating for K_p

$$\frac{d\ln K_p}{dT}=\frac{\Delta\hat{H}_R(T)}{\bar{R}T^2}\Rightarrow\int_{K_{p1}}^{K_{p2}} d\ln K_p=\ln\frac{K_{p2}}{K_{p1}}=\int_{T_1}^{T_2}\frac{\Delta\hat{H}_R(T)}{\bar{R}T^2}dT$$

- Can use this to find $K_p(T_2)$ if $K_p(T_1)$ known -- if we have information (e.g. tables) on heat of reaction
- For "small" ΔT, assume ΔH_R~constant

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

"small" ΔT when change in 2nd term below is "small" – so better when strongly exothermic or endothermic

- Otherwise

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

$$\cong\Delta\hat{H}_{R,0}+\sum\nu_i\left(a_iT+\frac{1}{2}b_iT^2+\frac{1}{3}c_iT^3\right)$$

$$\ln K_p\cong C+\frac{1}{\bar{R}}\left\{-\Delta\hat{H}_{R,T=0}/T+\sum\nu_i\left(a_i\ln T+b_iT/2+c_iT^2/6\right)\right\}$$

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K_c Temperature Dependence

- For TPG, we had

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

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

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

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

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

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

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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 $\Rightarrow$ TPG and $\bar{h}_i = \hat{h}_i$ and since K_f not function of f

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