How do we get $k_{eq}$ at different temperatures?

\[
\frac{d \ln k_{eq}}{dT} = \frac{\Delta H_{\text{rea}d}}{RT^2}
\]

Note that:

\[
\Delta H_{\text{rea}ct} = f(T) \text{ as well}
\]

\[
(\Delta H_{\text{rea}ct})_T = \left( \int_{T_{\text{ref}}}^T \sum \text{En}_i \Delta H_i \text{d}T \right)_{\text{rea}ctants} + (\Delta H_{\text{rea}ct})_{T_{\text{ref}}} + \left( \int_{T_{\text{ref}}}^T \sum \text{En}_j \Delta H_j \text{d}T \right)_{\text{products}}
\]

**Diagram:**

- Initial state (reactants)
- Transition state
- Final state (products)

**Equation:**

\[
\text{idea: } \frac{d \ln k_{eq}}{dT} = \frac{\Delta H_{\text{rea}x}}{RT^2} = \frac{f(T)}{RT^2}
\]

\[
\int_{T_{\text{ref}}}^T d \ln k_{eq} = \int_{T_{\text{ref}}}^T \frac{f(T)}{RT^2} \text{d}T
\]

$f(T)$ is usually some combination of polynomials.
B. More Concepts on Equilibrium

1. How do we get $k_{eq}$ at different temperatures?

$$\frac{\Delta \ln k_{eq}}{\Delta T} = \frac{\Delta H_{\text{react}}}{R T^2}$$

$$\left( \Delta H_{\text{react}} \right)_{T_2} = \left( \int_{T_2}^{T_1} E_i C_P \, dT \right)_{\text{reactants}} + \left( \int_{T_2}^{T_1} E_i C_P \, dT \right)_{\text{products}}$$

2. How do we do equilibrium when we have lots of species?

$$G_{\text{out}} = \left( \sum_i G_i \right)_{\text{out}}$$

$\Rightarrow$ chemical equilibrium occurs when $G_{\text{out}}$ is at a minimum!

$$dG_{\text{out}} = 0 = \sum (G_i \, dn_i)_{\text{out}} + \sum (n_i \, dG_i)_{\text{out}}$$

a. find $n_i$'s to minimize $G_{\text{out}}$ (constant $T$, $H$ varies)

b. find $n_i$'s and $T$ to minimize $G_{\text{out}}$ (constant $H$)
3. So what do you need to calculate chemical equilibrium?

\((\text{Input})\)

a. feed composition
b. pressure
c. energy level

\(1. \text{ Temperature}\)
\(2. \text{ Equilibrium}\)
\(c. \text{ heat loss calculated}\)

so if \(Y_{\text{feed}}\), \(P_{\text{tot}}\), \(T\) are specified,

\[
\left(\frac{dG}{dt}\right)_{\text{constant } P, T, \frac{Y}{Y_{\text{feed}}}} = 0
\]

\[\Rightarrow \text{guess } n_{i_{\text{out}}} \]
\[\Rightarrow \text{get } G_{i_{\text{out}}}\]
\[\Rightarrow \text{get } H_{i_{\text{out}}} \text{ level}\]
\[\Rightarrow \text{calculate } G\]

4. Constraints (i.e., boundary conditions or solution)

a. element balance on each element \(k\)

\[\sum (x_{ik} n_i)_{\text{feed}} = \sum (x_{ik} n_i)_{\text{out}}\]

b. energy balance (or constant \(T\))

5. Problems with using equilibrium codes

a. solid, liquid species \(\text{O}_2, \text{H}_2, \text{O}_2, \text{Al}_2\text{O}_3\)

(b. ideal gas

c. need data for all relevant species

6. All major codes (EDWARDS, NASA-Lewis, StanJan) use minimization of Gibbs's free energy
\[ \frac{h}{RT} = \frac{21}{2} + \frac{22}{3} T^2 + \frac{23}{4} T^3 + \frac{24}{5} T^4 + \frac{25}{6} T^5 \]

\[ \frac{\partial H}{\partial T} = \rho \partial T + \left[ \frac{\partial V}{\partial T} \right] _P \] Balzhiser p. 167,

\[ PV = RT \]

\[ \frac{y}{P} = \frac{RT}{P} \]

\[ T \frac{\partial y}{\partial T} \bigg|_P = \frac{RT}{P} = \frac{y}{P} \]

so for ideal gas, no change in enthalpy with pressure!