Chapter 4: Thermochemistry

Enthalpy

Chemical bonds represent internal energy
Chemical reaction means a change in internal energy
Exothermic Reaction $\rightarrow$ Release Energy $\rightarrow$ produced heat does work
Quantity of energy change: ΔH constant pressure
ΔU constant volume (for gases)

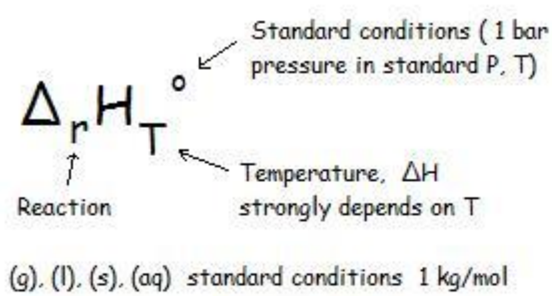
Focus on ΔH

ΔH : is a function of state, only depends on initial and final states

Initial: $A + B \rightarrow C + D$

$T_i, P_i \qquad T_f, P_f$

$\rightarrow$ Calculate in little steps: add them up



$\Delta_r H_T^o$, is defined for reaction as written

a) $3H_{2\ (g)} + N_{2\ (g)} \rightarrow 2NH_{3\ (g)} \qquad \Delta_r H_{298.15}^o(a)$

b) $\frac{3}{2}H_{2\ (g)} + \frac{1}{2}N_{2\ (g)} \rightarrow NH_{3\ (g)} \qquad \Delta_r H_{298.15}^o(b) = \frac{1}{2}\Delta H(a)$

Heat of formation/enthalpy of formation

$\Delta_f H_{298.15}{}^o$ (molecule)

: heat involved in forming 1 mole of molecule from elements in their "elemental state

$\Delta_f H_{298.15}{}^o \left(NH_3\right)$ $\quad \frac{3}{2}H_{2\ (g)} + \frac{1}{2}N_{2\ (g)} \rightarrow NH_{3\ (g)}$

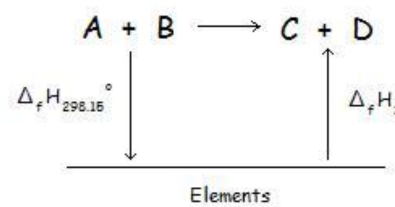
NOT $\quad 3H_{2\ (g)} + N_{2\ (g)} \rightarrow 2NH_{3\ (g)}$

$\Delta_f H_{298.15}{}^o \left(C_2H_5OH\right)$ $\quad 2C_{\ (s)} + 3H_{2\ (g)} + \frac{1}{2}O_{2\ (g)} \rightarrow C_2H_5OH_{\ (l)}$

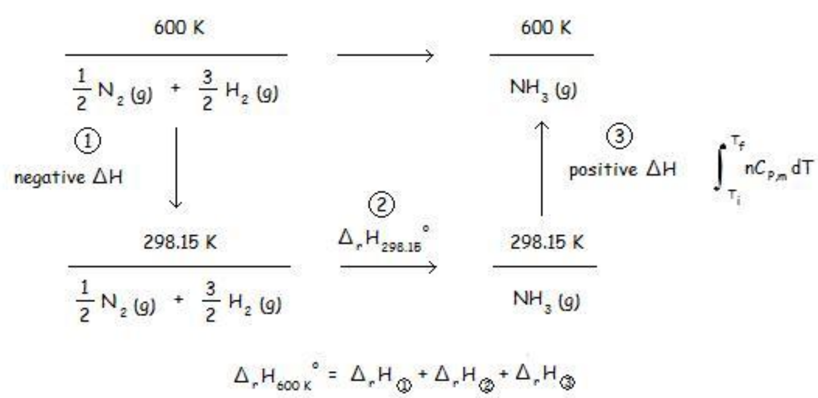
Elemental states:

$H_{2\ (g)}, N_{2\ (g)}, O_{2\ (g)}, F_{2\ (g)}, Li_{\ (s)}, B_{\ (s)}, P_{\ (s)}$ Tabulated in back of book 4.1, 4.2

From $\Delta_f H_{298.15}{}^o$, I can calculate $\Delta_r H_{298.15}{}^o$ for any reaction



If I know $C_{P,m}$ for any molecule, I can calculate $\Delta_r H_T{}^o$ at any T



$C_P{}^{\text{reactant}}$ of $\frac{1}{2}N_2 + \frac{3}{2}H_2 = \frac{1}{2}C_{P,m}(N_2) + \frac{3}{2}C_{P,m}(H_2)$

$\rightarrow C_P$ depends on T in general

$$\Delta H\left(T_i \rightarrow T_f\right) = \int_{T_i}^{T_f} C_P dT$$

If C_P is assumed constant $\Delta H = C_P\left(T_f - T_i\right)$

Systematic approach to $\Delta_r H_T^o$ (a formula)

$$n_A A + n_B B \rightarrow n_C C + n_D D \qquad n_I : \text{stoichiometric coefficient}$$

$$n_C C + n_D D - n_A A - n_B B = 0$$

$$\nu_I = n_I \text{ for products } \nu_I > 0$$

$$\nu_I = -n_I \text{ for reactants } \nu_I < 0 \qquad I = A, B, C, D$$

Reaction : $\sum_I \nu_I I = 0$

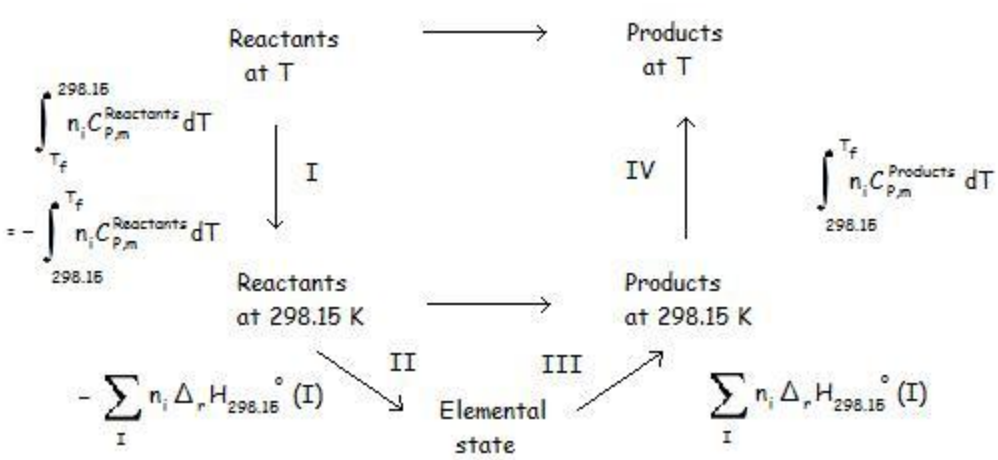
If I know ν_I , $C_{P,m}$ and $\Delta_f H_{298.15}^{\ o}\left(I\right)$ for each molecule I

$$\Delta_r H_T^{\ o} = \int_{298.15}^{T} \sum_I \nu_i C_{P,m,I}\, dT + \sum_I \nu_I \Delta_f H_{298.15}^{\ o}(I)$$

Steps I + III (in Joules) Step II + IV (in KJ)

(convert units before adding!)

Derivation of formula:



If C_P depends on T (power series)

$$C_{P,m}^{I} = a^I + b^I \frac{T}{K} + c^I \frac{T^2}{K^2}$$

$$\rightarrow \int C_P dT : \int_{298.15}^{T} \left[\left(\sum_I \nu_I a^I \right) + \left(\sum_I \nu_I b^I \right) T + \left(\sum_I \nu_I c^I \right) T^2 \right] dT$$

Relation Between $\Delta_r U_T^o$ and $\Delta_r H_T^o$

$\Delta_r H_T{}^o$: constant pressure processes

$\Delta_r U_T{}^o$: constant volume process

$H = U + PV$ by definition

$U = H - PV$

$\Delta U = \Delta H - \Delta(PV)$

Apply to reaction energies at constant T

$$\Delta_r U_T{}^o = \Delta_r H_T{}^o - \Delta(PV) \qquad \Delta(PV) = \left(n_{gas}^{\text{Products}} - n_{gas}^{\text{Reactant}} \right) RT$$

Eg.

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$$

Reactants: $PV = \frac{3}{2} RT$

Products: $PV = 0$

$$\Delta_r U_T{}^o = \Delta_r H_T{}^o - \left(-1 - \frac{1}{2} \right) RT$$

$$\Delta_r U_T{}^o = \Delta_r H_T{}^o + \frac{3}{2} RT$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)}$$

Reactants: $PV = \frac{3}{2} RT$

Products: $PV = \frac{1}{2} RT$

$$\Delta_r U_T{}^o = \Delta_r H_T{}^o - \left(1 - 1 - \frac{1}{2} \right) RT$$

$$\Delta_r U_T{}^o = \Delta_r H_T{}^o + \frac{1}{2} RT$$

Ions in Solution

We would like to use heats of formation for reactions involving ions in solution

Elementary definition of reactions for $\Delta_f H$ ions:

$$Na_{(s)} + H_2O_{(l)} \rightarrow Na^+{}_{(aq)} + e^{-1}{}_{(aq)}$$

$$e^-{}_{(aq)} + \frac{1}{2} Cl_{2(g)} + H_2O_{(l)} \rightarrow Cl^-{}_{(aq)}$$

In reality such half reactions do not occur, e.g.

$$Mg_{(s)} + H_2O_{(l)} \rightarrow Mg^{+2}{}_{(aq)} + H_{2(g)} + 2OH^-{}_{(aq)}$$

NOT $Mg_{(s)} + H_2O_{(l)} \rightarrow Mg^{+2}{}_{(aq)} + 2e^-{}_{(aq)}$

No such “half reactions” actually occur

Define artificial reference point:

$$\frac{1}{2}H_{2(g)} \rightarrow H^{+}{}_{(aq)} + e^{-}{}_{(aq)} \qquad \Delta_r H_T{}^{o} = 0 \text{ for any } T \ (??)$$

$$HCl_{(g)} \rightarrow H^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \qquad \Delta H_I$$

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(aq)} \rightarrow HCl_{(g)} \qquad \Delta H_{II}$$

$$\frac{1}{2}H_{2(g)} \rightarrow H^{+}{}_{(aq)} + e^{-}{}_{(aq)} \qquad \Delta H_{III} = 0$$

$$\frac{1}{2}Cl_{2(g)} + e^{-} \rightarrow Cl^{-}{}_{(aq)} \qquad \text{Add reactions } I + II + III = IV$$

$$\Delta_f H_{298.15}{}^{o}\left[Cl^{-}{}_{(aq)}\right] = \Delta_r H_I + \Delta_r H_{II} + \Delta_r H_{III}$$