

How do you calculate ΔH for a given phase change/chem rxn? (i.e. $\Delta_r H$)

Chem 115
Hanson Ch. 9

(1) Use def'n: $\Delta_r H = \Delta_r U + p \Delta V$

↑
Estimate with BDE's (Chap. 5)

What about ΔV ?

FACT: At 25°C , 1 g of $\text{H}_2\text{O}_{(l)}$ has $V_l = 1 \text{ mL}$.

" " " " " $\text{H}_2\text{O}_{(g)}$ " $V_g = 10^3 \text{ mL}$

In general, $V = V_s + V_l + V_g \cong V_g$

$\Rightarrow \Delta V \cong \Delta V_g$

and $pV_g = nRT \Rightarrow V_g = \frac{nRT}{p}$

so $\Delta V_g = V_{g,f} - V_{g,i} = \frac{n_f RT_f}{p_f} - \frac{n_i RT_i}{p_i}$

but remember that we are assuming

(1) thermal equilibrium ($T_i = T_f \equiv T$)

(2) mechanical " ($p_i = p_f \equiv p$)

so $\Delta V_g = \frac{RT}{p} (n_f - n_i)$ or $\Delta V_g = \frac{RT}{p} \Delta n_g$

and $p \Delta V = RT \Delta n_g = \Delta_r H - \Delta_r U$ (Chap. 9 hwk)

(2) Use experimental H values for each reactant and product.

Problem: We don't know absolute values for H (as is the case with any potential energy)

How do we get around this?

(a) Standard State of an Element: Its most stable form (at $T = 298 \text{ K}$) and $p = 1 \text{ bar}$

(b) Standard Enthalpy of Formation of X ($\Delta_f H^\circ(X)$): The standard enthalpy change ($\Delta_r H^\circ$) for the rxn in which 1 mol of X is formed from elements in their standard states

(c) Imagine a two-step process:

reactants \rightarrow elements in their standard states

elements in their standard states \rightarrow products

In general, for $aA + bB \rightarrow cC + dD$

$$\Delta_r H^\circ = c \Delta_f H^\circ(C) + d \Delta_f H^\circ(D) - a \Delta_f H^\circ(A) - b \Delta_f H^\circ(B)$$