SEQUENCES OF REACTIONS; HESS'S LAW

The change in state of a system produced by a specified chemical reaction is definite. The corresponding enthalpy change is definite, since the enthalpy is a function of the state. Thus, if we transform a specified set of reactants to a specified set of products by more than one sequence of reactions, the total enthalpy change must be the same for every sequence. This rule, which is a consequence of the first law of thermodynamics, was originally known as Hess's law of constant heat summation. Suppose that we compare two different methods of synthesizing sodium chloride from sodium and chlorine.

Method 1.

$$\begin{aligned}
\mathrm{Na(s)} + \mathrm{H_2O(l)} &\longrightarrow \mathrm{NaOH(s)} + \tfrac{1}{2}\mathrm{H_2(g)}, & \Delta H &= -139.78\ \mathrm{kJ/mol} \\
\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} &\longrightarrow \mathrm{HCl(g)}, & \Delta H &= -\ \ 92.31\ \mathrm{kJ/mol} \\
\mathrm{HCl(g)} + \mathrm{NaOH(s)} &\longrightarrow \mathrm{NaCl(s)} + \mathrm{H_2O(l)}, & \Delta H &= -179.06\ \mathrm{kJ/mol}
\end{aligned}$$

Net change: $\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{NaCl(s)}$, $\Delta H_{\mathrm{net}} = -411.15\ \mathrm{kJ/mol}$

Method 2.

$$\begin{aligned}
\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} &\longrightarrow \mathrm{HCl(g)}, & \Delta H &= -\ \ 92.31\ \mathrm{kJ/mol} \\
\mathrm{Na(s)} + \mathrm{HCl(g)} &\longrightarrow \mathrm{NaCl(s)} + \tfrac{1}{2}\mathrm{H_2(g)}, & \Delta H &= -318.84\ \mathrm{kJ/mol}
\end{aligned}$$

Net change: $\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{NaCl(s)}$, $\Delta H_{\mathrm{net}} = -411.15\ \mathrm{kJ/mol}$

Relación entre ΔH_r y ΔU_r

$$H = U + PV$$

$$\Delta H_r = \Delta U_r + \Delta(PV)$$

para los gases ideales; $\Delta(PV) = \Delta(nRT)$

$$\Delta H_r = \Delta U_r + \Delta(nRT)$$

asumiendo que T = cte

$$\Delta H_r = \Delta U_r + \Delta n_{(gases)} RT$$

$$\Delta n_{(gases)} = n_{prod} - n_{react}$$

$$\Delta U^0_{r298.15K} = \Delta H^0_{r298.15} - \Delta n_{(gases)} RT$$

Usando el ejemplo de la combustión del ácido benzoico (ver ecuación balanceada):

$$\Delta n_{(gases)} = 7mol - \frac{15}{2}mol = -\frac{1}{2}mol$$

$$\Delta U^0_{r298.15} = -3227260J/mol - \left(-\frac{1}{2}\right)(8.314J/mol)(298.15K)$$

$$\Delta U^0_{r298.15} = -3226020J/mol$$

$$\Delta U^0_{r298.15} = (-3226020J/mol)\left(\frac{1cal}{4.184J}\right)\left(\frac{1mol}{122g}\right) = -6319.97\frac{cal}{g}$$

Relación entre la entalpía de reacción y la temperatura

Si C_p varía con la temperatura, por ejemplo: $C_p = a + bT + \frac{c}{T^2}$

$$dH = C_p dT = \left(a + bT + \frac{c}{T^2} \right)$$

$$\int_{H(T1)}^{H(T2)} dH = \int_{T1}^{T2} \left(a + bT + \frac{c}{T^2} \right)$$

$$\int_{H(T1)}^{H(T2)} dH = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c(\frac{1}{T_2} - \frac{1}{T_1})$$

$$H(T_2) = H(T_1) + \left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c(\frac{1}{T_2} - \frac{1}{T_1}) \right]$$