STATISTICAL MOLECULAR THERMODYNAMICS

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Video 5.10

Standard Enthalpy

STANDARD ENTHALPY OF REACTION

 $\Delta_{\rm r} H$ is *extensive*; its value depends on the number of moles of the reacting species

To facilitate tabulation, the International Union of Pure and Applied Chemistry created the *standard enthalpy of reaction*, which is *intensive*

^o implies one mole of a specified reagent and all reactants and products in their standard states at a given temperature. (standard states are chosen by convention, for example, for a gas it is a pressure of one bar)

E.g.,
$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H^\circ = -393.5 \text{ kJ} \cdot \text{mol}^{-1}$$

(one mole of C is combusted) (at 298 K) (intensive)
Then, $2C(s) + 2O_2(g) \longrightarrow 2CO_2(g) \quad \Delta_r H = 2\Delta_r H^\circ = -787 \text{ kJ}$
(extensive)

STANDARD MOLAR ENTHALPY OF FORMATION

The standard enthalpy of reaction to form one mole of a substance from its constituent elements in their naturally occurring elemental forms defines the intensive *standard molar enthalpy of formation*,

indicates all reactants and products in their conventional standard states

$$H_{2}(g) + \frac{1}{2}O_{2}(g) \longrightarrow H_{2}O(l) \quad \Delta_{f}H^{\circ} = -285.8 \text{ kJ} \cdot \text{mol}^{-1}$$
(at 298.15 K)

Standard-state phases at 1 bar and 298.15 K

One mole of $H_2O(I)$ is 285.8 kJ downhill in enthalpy from its constituent elements

THERMOCHEMICAL ABBREVIATIONS

subscript meaning vap — vaporization, evaporation sub —— sublimation fus — melting, fusion trs —— transition between phases mix — mixing of fluids or gases ads — adsorption c —— combustion f — formation r — reaction

ELEMENTAL HEATS OF FORMATION

To assign specific values for $\Delta_{f}H^{\circ}$, the values of $\Delta_{f}H^{\circ}$ for *pure elements* in their *most stable forms* at *one bar* and the *temperature of interest* is set to *zero*.

298 K:
$$H_2(g) \quad \Delta_f H^\circ = 0 \text{ kJ } \cdot \text{mol}^{-1}$$

 $O_2(g) \quad \Delta_f H^\circ = 0 \text{ kJ } \cdot \text{mol}^{-1}$
 $Cl_2(g) \quad \Delta_f H^\circ = 0 \text{ kJ } \cdot \text{mol}^{-1}$
 $Br_2(g) \quad \Delta_f H^\circ = 30.907 \text{ kJ } \cdot \text{mol}^{-1}$
 $I_2(g) \quad \Delta_f H^\circ = 62.438 \text{ kJ } \cdot \text{mol}^{-1}$
 $C(\text{diamond}) \quad \Delta_f H^\circ = 1.897 \text{ kJ } \cdot \text{mol}^{-1}$

Using $\Delta_{\rm f} H^{\rm o}$ to Get $\Delta_{\rm r} H$

One can use Hess' law, together with the standard enthalpies of formation for each of the reactants and products, to compute a heat of reaction at a temperature of interest, e.g., 298 K:



$\Delta_{\mathbf{r}} H = \Delta_{\mathbf{f}} H^{\circ}(\text{products}) - \Delta_{\mathbf{f}} H^{\circ}(\text{reactants})$ $\Delta_{\mathbf{r}} H = \left(y \Delta_{\mathbf{f}} H^{\circ}[\mathbf{Y}] + z \Delta_{\mathbf{f}} H^{\circ}[\mathbf{Z}] \right) - \left(a \Delta_{\mathbf{f}} H^{\circ}[\mathbf{A}] + b \Delta_{\mathbf{f}} H^{\circ}[\mathbf{B}] \right)$

Relating $\Delta_r H$ Values at Different TTo convert $\Delta_r H$ from T_1 (e.g., 298 K) to T_2 requires C_P $\Delta_r H(T_2)$ $\Delta_{\rm r} H(T_2) = \Delta H_1 + \Delta H_2 + \Delta H_3$ T_{2} desired (note sign and order of limits) Path : Path 3 $\Delta H_1 = -\int_{T_1}^{T_2} C_P (\text{reactants}) \, dT$ $\Delta H_2 = \Delta_r H(T_1)$ known $\Delta_{\rm r} H(T_1)$ $\Delta H_3 = \int_{T_1}^{T_2} C_P (\text{products}) \, dT$ T_1 ➤ T₁ Path 2 $\Delta_{\rm r} H(T_2) = \Delta_{\rm r} H(T_1) + \int_{T_2}^{T_2} \left[C_P(\text{products}) - C_P(\text{reactants}) \right] dT$