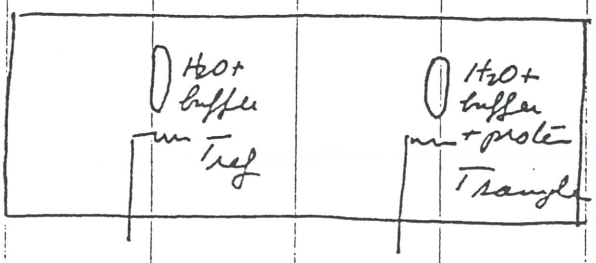
Differential Scanning Calorimeter



(1) Heat both reference and sample to meet:

$$T_{ref} = T_{sample}$$

(2) Scan temperature, slowly varying T

(3) $$\left(\frac{dQ_p^{ref}}{dT}\right) = C_p^{ref}$$

$$\frac{dQ_p^{sample}}{dT} = C_p^{sample}$$

(4) Excess heat capacity $= C_p^{sample} - C_p^{ref}$

Standard Enthalpy of Formation of a Compound

→ If reaction involves the formation of a compound from its elements, then the ΔH_{RX} is called the enthalpy of formation of the compound, ΔH_f

e.g.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

$$\Delta H_{RX} = \Delta H_f(H_2O(g)) = H_{H_2O(g)}(T,P) - H_{H_2(g)}(T,P) - \tfrac{1}{2}H_{O_2(g)}(T,P)$$

If $T = 298K$, $P = 1$ atm,

then $\Delta H_f = \Delta H_f^\circ$ of substance. ≡ standard enthalpy of formation

→ To avoid any ambiguity in the choice of the state of the elements, one picks the most stable physical state (solid, liquid, or gas) of the element under the standard conditions of temperature and pressure.

H_2	gas (at 298K and 1 atm)
O_2	gas at 298K and 1 atm
C	C(s) graphite
N_2	gas

e.g. ΔH_f° of $CH_4(g)$ is just ΔH_{RX} (298K, 1 atm)

for the reaction

$$C(s) + 2H_2(g) \longrightarrow CH_4(g).$$

$$\Delta H^\circ_f = -74.8 \text{ kJ/mol}$$

→ ΔH°_{RX}'s are readily derived from ΔH°_f of reactants and products

Chemical equation

$$\underline{a}\,A + \underline{b}\,B \longrightarrow \underline{c}\,C + \underline{d}\,D$$

$$\Delta H^\circ_{RX} = \underline{c}\,\Delta H^\circ_{fC} + \underline{d}\,\Delta H^\circ_{fD} - \underline{a}\,\Delta H^\circ_{fA} - \underline{b}\,\Delta H^\circ_{fB}$$

Can express ΔH_f°'s into H's of reactants and products and the H's of the elements of which each reactant and product is composed.

Because elements are conserved during a chemical reaction, the enthalpy terms from the elements cancel out

→ Standard enthalpy of formation of selected compounds and substances of biochemical importance are given in Table 2-3 (page 63-64) of text.

$$\Delta H^\circ_{RX} = \sum \Delta H^\circ_f (\text{products}) - \sum \Delta H^\circ_f (\text{reactants})$$

Reaction Heats at Other Temperatures from ΔH°_{RX}

Since $\left(\frac{\partial H}{\partial T}\right)_P = C_p$; $(dH)_p = C_p\, dT$ at constant Pressure

$$d(\Delta H)_p = \Delta C_p\, dT$$

where $\Delta C_p = \sum C_p(\text{products}) - \sum C_p(\text{reactants})$

Integrating, we have

$$\boxed{\Delta H^\circ_T - \Delta H^\circ_{298} = \int_{298}^{T} \Delta C_p\, dT}$$

Second Law of Thermodynamics. Concept of ENTROPY

First Law relates heat, work and energy

$$dE = dQ + dW$$

merely a statement of conservation of energy

DOES NOT in fact say whether the process will occur; that is, tell us if a given process is spontaneous.

Second Law accomplishes this!