

CEM 882

Lecture Notes 5

Wality



system \equiv solute + solvent

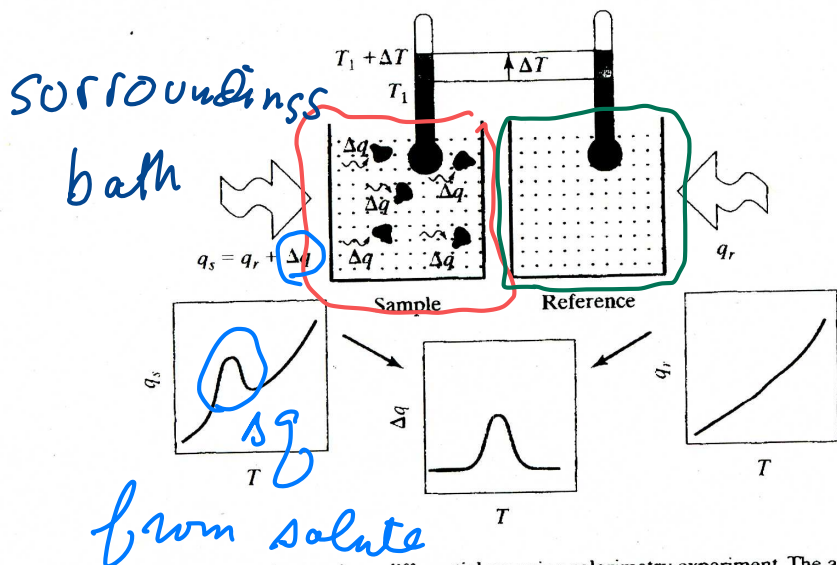


Figure 2.7 Experimental setup for a differential scanning calorimetry experiment. The amount of heat required to increase the temperature by the same increment (ΔT) of a sample cell (q_s) is higher than that required for the reference cell (q_r) by the excess heat absorbed by the molecules in the sample (Δq). The resulting DSC scans with the reference subtracted from the sample shows how this excess heat changes as a function of temperature.

$$c_p = \frac{q}{\Delta T} \text{ as a function of } T$$

Very useful for measuring large changes in state of solute

Heat is added to calorimeter slowly so consider reversibly so differential calculus can be used

$$C_p = \frac{\delta q}{\delta T} \approx \frac{dH}{dT} \approx T \frac{dS}{dT}$$

heat capacity of solution at constant $p = 1 \text{ atm}$

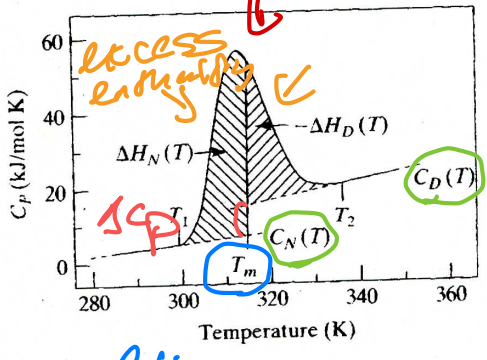
$$dS = \frac{C_p}{T} dT$$

$$\int_{T_1}^{T_2} \frac{dH}{dT} dT = \int_{T_1}^{T_2} dH = \Delta H$$

After reference subtraction

Calorimetry of protein unfolding (100-150 residues)

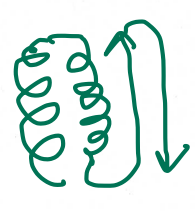
Figure 2.8 DSC for protein denaturation shows the heat capacity (C_p) changing from that of the native form [$C_N(T)$] to that of denatured form [$C_D(T)$]. At the point of transition is the excess heat capacity associated with denaturation. The integrated areas under the curve from T_1 (fully native) to T_2 (fully denatured) is the enthalpy for denaturation. At the midpoint temperature (T_m), the protein is half native and half denatured; thus the associated enthalpies for the folded native [$\Delta H_N(T)$] and denatured [$\Delta H_D(T)$] protein are equal and of opposite signs. [Adapted from S.-I. Kidokoro and A. Wada (1987), *Biopolymers* 26, 213-229.]



from native to denatured thermodynamic states

Native $\equiv N \equiv$ folded

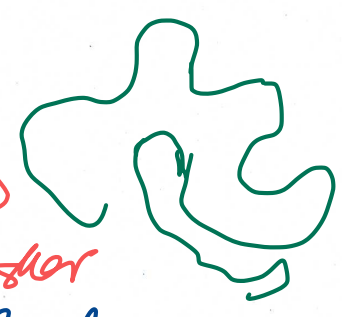
Denatured $\equiv D \equiv$ unfolded



Mostly Native at lower T



W is much higher \Rightarrow



Mostly denatured at

Narrow distribution of structures that are similar to one another

higher T . rapidly into irregular structures that are different from one another and struts

Melting enthalpy ΔH_m is excess enthalpy near T_m

$$\Delta H_m \approx \frac{(C_p^{\text{excess}})(\Delta T)}{2} \approx \frac{\left(40 \frac{\text{kJ}}{\text{mole-K}}\right)(20\text{K})}{2}$$

$$\approx 400 \text{ kJ/mole}$$

$$T_m \approx 315 \text{ K}$$

$$\Delta S_m \approx \frac{\Delta H_m}{T_m} \approx 1250 \frac{\text{J}}{\text{mole-K}} \approx 10 \frac{\text{J}}{\text{mole-K}} \text{ per residue}$$

$$C_{p,d} > C_{p,n} \Rightarrow \Delta C_p = C_{p,d}(T_m) - C_{p,n}(T_m) \approx$$

$$8 \text{ kJ/mole-K} = \Delta C_p^0$$

Calculate $\Delta H, \Delta S, \Delta G$ (d-n) at

temperatures other than T_m

$$\Delta H = H_d - H_n$$

At T_m

$$\Delta S = S_d - S_n$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

$$\Delta G_m = \Delta H_m - T_m \Delta S_m = 0$$

$$C_{p,n}(T) = C_n^{\circ} + C' (T - T_m) = C_n^{\circ} + C' \Delta T$$

at T_m slope

$$C_{p,d}(T) = C_d^{\circ} + C' \Delta T$$

same linear dependence $\Delta C_p = C_d^{\circ} - C_n^{\circ}$

$$H_n(T) = \int_{T_m}^T (C_n^{\circ} + C' \Delta T) dT - \frac{\Delta H_m}{2}$$

$$H_d(T) = \int_{T_m}^T (C_d^{\circ} + C' \Delta T) dT + \frac{\Delta H_m}{2}$$

$$S_n(T) = \int_{T_m}^T \left(\frac{C_n^{\circ} + C' \Delta T}{T} \right) dT - \frac{\Delta S_m}{2}$$

$$S_d(T) = \int_{T_m}^T \left(\frac{C_d^{\circ} + C' \Delta T}{T} \right) dT + \frac{\Delta S_m}{2}$$

$$\Delta H(T) = H_d(T) - H_n(T) = \int_{T_m}^T \Delta C_p dT + \Delta H_m$$

$\Delta T = +20 \text{ K}$ $\Delta T = -20 \text{ K}$ $\Delta H \approx 560 \text{ kJ/mole}$ $\Delta H \approx 290 \text{ kJ/mole}$

$$\Delta H \approx \Delta C_p^{\circ} \Delta T + \Delta H_m$$

$$\Delta S = S_d(T) - S_n(T) = \int_{T_m}^T \frac{\Delta C_p^{\circ}}{T} dT + \Delta S_m$$

$$= \Delta C_p^{\circ} \ln \left(\frac{T}{T_m} \right) + \frac{\Delta H_m}{T_m} = \Delta C_p^{\circ} \ln \left(1 + \frac{\Delta T}{T_m} \right) + \frac{\Delta H_m}{T_m}$$

$\Delta T = +20 \text{ K}$
 $\Delta S \approx 18 \text{ J/mole} \cdot \text{K}$
 $\Delta T = -20 \text{ K}$

$\Delta S \approx 650 \text{ J/mole} \cdot \text{K}$

$\approx \Delta C_p^{\circ} \left(\frac{\Delta T}{T_m} \right) + \frac{\Delta H_m}{T_m} = \frac{\Delta T}{T_m} \text{ for } \frac{\Delta T}{T_m} \ll 1$

$\Delta S \approx 650 \text{ J/mole} \cdot \text{K}$

$$\Delta G = \Delta H - T\Delta S = \Delta C_p^{\circ} \Delta T \left(1 - \frac{T}{T_m}\right) + \Delta H_m \left(1 - \frac{T}{T_m}\right)$$

$$= \left(\Delta C_p^{\circ} \Delta T + \Delta H_m \right) \left(-\frac{\Delta T}{T_m} \right)$$

> 0 for
 $\Delta T > 0$

< 0 for
 $\Delta T < 0$

400 $\frac{\text{kJ}}{\text{mole}}$

$$\Delta T = -20 \text{ K} \Rightarrow \Delta G = +15 \frac{\text{kJ}}{\text{mole}}$$

295K

$$\Delta T = +20 \text{ K} \Rightarrow \Delta G = -35 \frac{\text{kJ}}{\text{mole}}$$

335K