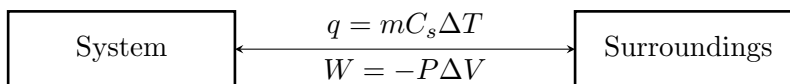**Calorimetry Constant Volume**

Consider a reaction occurring in a *bomb calorimeter* (operates at constant-volume). What is the amount of work done? What is the change in energy?

$$\boxed{\text{System}} \xleftrightarrow{\substack{q = mC_s\Delta T \\ W = -P\Delta V}} \boxed{\text{Surroundings}}$$

By measuring the heat transferred into the surroundings, $\Delta_r U$ can be determined:

$$\Delta U = q_V + W$$
$$\Delta U = q_V - P\Delta V \qquad\qquad (\Delta V = 0,\ W = 0)$$
$$\Delta U = q_V = q_{rxn}$$

Heat lost by the reaction is equal in magnitude but opposite in sign to the heat gained by the surrounding solution (calorimeter).

$$q_{rxn} = -q_{cal}$$

Consider three subsystems:

1. Reactants in calorimeter.

2. Inner bath water.

3. Calorimeter vessel.

Then we have that

$$\Delta U = \underbrace{\frac{m_s}{M_s}\Delta_c U}_{sample} + \underbrace{\frac{m_{H_2O}}{M_{H_2O}}C_{P,m}(H_2O, \ell)\Delta T}_{water\ bath} + \underbrace{C_{cal}\Delta T}_{vessel} = 0$$

Experiments to determine ΔU:

- Known quantities:

  - Mass and molar mass of the sample.
  - Mass and heat capacity of water.
  - Heat capacity of calorimeter (needs to be determined in a separate experiment)

- Measured quantities:

  - Change in temperature.

As stated previously, the bomb calorimetry experiments provides $\Delta_r U$ through the measurement of the heat evolved during the combustion reaction carried out at constant volume, q_V.

$$\Delta H = \Delta U + P\Delta V \qquad P\Delta V = \Delta n R T$$

where Δn is the change in the number of gas molecules as the reaction proceeds from reactants to products.

$$\Delta_r H = \Delta_r H + \Delta n R T$$

for reactions involving only solids or liquids: $\Delta_r H \approx \Delta_r U$.

Example 1. The dipeptide glycylglycine ($C_4H_8O_3N_2$) has a standard enthalpy of combustion of -1969 kJ/mol. Calculate q, W, ΔU and ΔH when 10.0 g of glycine are burned at $T = 298$ K and a constant pressure of 1.00 bar. Assume the combustion products are carbon dioxide gas, nitrogen gas, and liquid water. The chemical equation for the combustion is:

$$C_4H_8O_3N_{2(s)} + \frac{9}{2}O_{2(g)} \rightarrow N_{2(g)} + 4\,CO_{2(g)} + 4\,H_2O_{(\ell)}$$
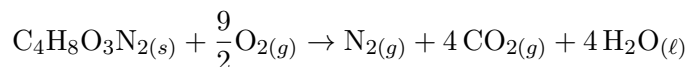
We first calculate ΔH_c, which is the same as q_c:

$$\Delta H_c(C_4H_8O_3N_2) = q_c(C_4H_8O_3N_2) = \frac{(-1969 \text{ kJ/mol})(10.0 \text{ g})}{132.12 \text{ g/mol}} = -149.0 \text{ kJ}$$

Then we calculate ΔU_c, which is given by $\Delta H_c(C_4H_8O_3N_2) - \Delta nRT$

$$\Delta U_c(C_4H_8O_3N_2) = (-149.03 \text{ kJ}) - \left[\left(\frac{1}{2} \times 0.0757 \text{ mol}\right) \times (8.314 \text{ J/mol K}) \times (298 \text{ K})\right] = -149.12 \text{ kJ}$$

Then work W_c is given by

$$W_c = -P_{ext}\Delta V = (-149.12 \text{ kJ}) - (8.314 \text{ J/mol K})(298 \text{ K})\left(\frac{1}{2} \times 0.0757 \text{ mol}\right) = -93.78 \text{ J}$$

Calorimetry: Constant Pressure

In the laboratory, most chemical and physical processes are carried out under *constant pressure* rather than constant volume. Measure the heat flow at *constant pressure*:

$$\Delta H_{rxn} = q_{rxn}$$

If the specific heat capacity of the solution is known, normally assumed to be that of water, q_s can be calculated using

$$\Delta H = q_{rxn} = q_s$$

Consider three subsystems

1. Reactants in calorimeter.

2. Inner water bath.

3. Calorimeter vessel.

Then

$$\Delta H^\circ = \underbrace{\frac{m_s}{M_s}\Delta_s H^\circ}_{sample} + \underbrace{\frac{m_{H2O}}{M_{H_2O}}C_{P,m}(H_2O, \ell)\Delta T}_{water\ bath} + \underbrace{C_{cal}\Delta T}_{vessel} = 0$$

Example 2. In a constant pressure calorimeter, 33.3 mL of 0.100 M $AgNO_3$ is mixed with 33.3 mL of 0.100 M HCl. The reaction $Ag^+_{(aq)} + Cl^-_{(aq)}$ takes place. The temperature of the reactants was 25.60°C and the final temperature was 26.47°C. Calculate the molar enthalpy change for this reaction.

Since $n(AgNO_3) = n(HCl) = (0.0333 \text{ L})(0.100 \text{ M}) = 0.00333$ mol, then

$$q_s = m_sC_s\Delta T = (2 \text{ g})(33.3 \text{ J/g °C})(4.181)(26.47 - 25.6 \text{ °C}) = 242.2 \text{ J}$$

and so $q_{rxn} = -242.2$ J. Then for molar enthalpy, divide by the number of moles.

$$\Delta H_{rxn} = -\frac{242.2}{0.00333} = -72.7 \text{ kJ/mol}$$

as required.

Differential Scanning Calorimetry

A thermal analysis technique in which the difference of the amount of heat required (or removed) to increase (decrease) the temperature of a sample compared to the reference material are measured while the temperature is varied.
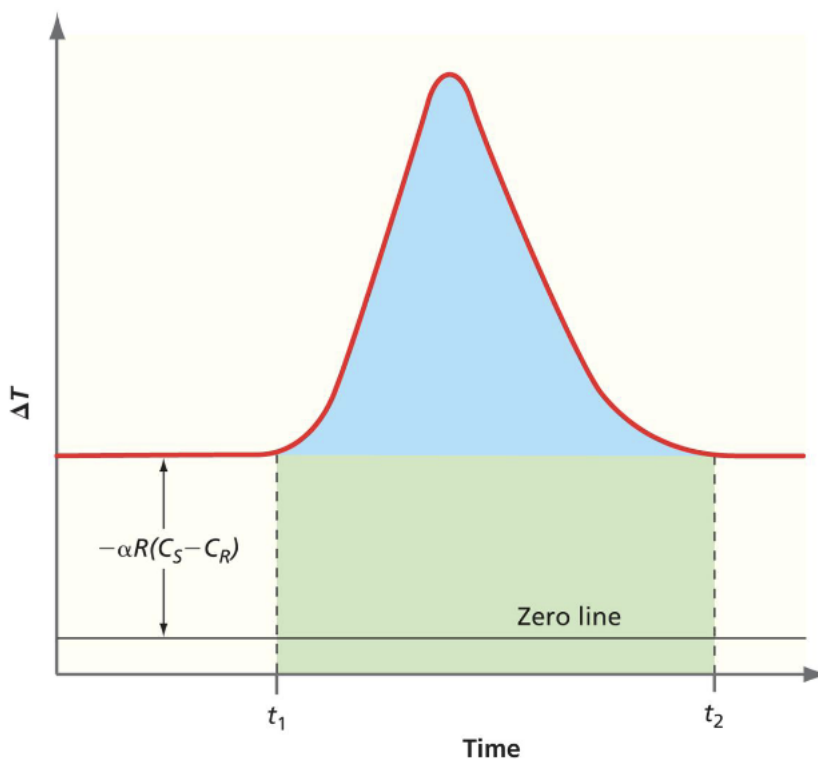
Used to study chemical changes in:

- Polymer cross-linking

- Melting

- Unfolding of protein molecules.

Heat is increased linearly with time:
$$T = T_0 + \alpha t$$

The graph illustrates the change during an exothermic process, assuming that the heat capacities of the sample and reference point stay constant.

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- Blue Area: proportional to heat associated with the process of interest.

- Green Area: arises from the difference in heat capacities of sample and reference.
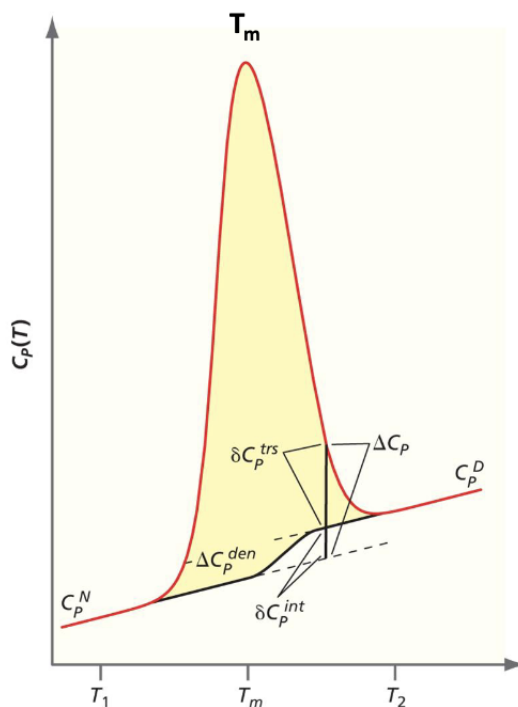
DSC For Polymers
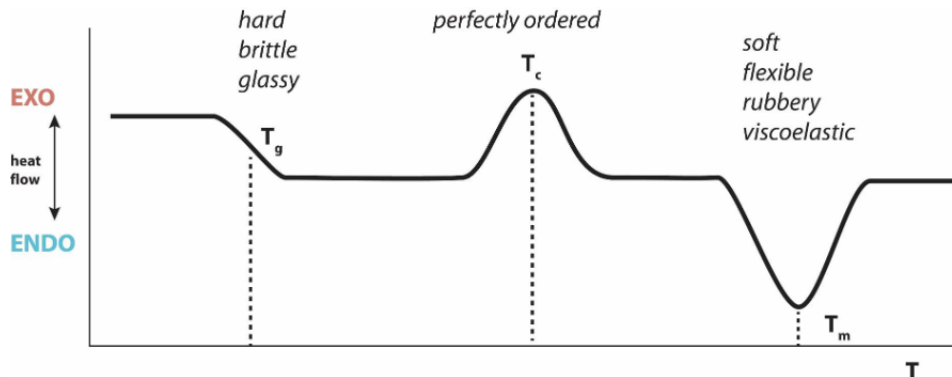
DSC has been implemented to study the temperature range over which proteins denature (unfold). The heat capacity of denaturation is given by

$$\Delta C_P^{den} = C_P^D - C_P^N$$

Typically, $C_P^D > C_P^N$ because of increased vibrational motions and more exposed amino and residuals that interact with water molecules.

$$\Delta C_P(T) = \delta C_P^{int} + \delta C_P^{trs}$$

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Tutorial Problems

Question 1. *Benzoic acid (C_6H_5COOH), 1.35 g is reacted with oxygen in a constant volume calorimeter to form $H_2O_{(\ell)}$ and $CO_{2(g)}$. The mass of the water in the inner bath is 1.24×10^3 g. The temperature of the calorimeter and its content rise 3.45 K as a result of this reaction. Calculate the calorimeter constant. Note that the standard enthalpy of combustion of benzoic acid (at 298 K) is -3228.0 kJ/mol.*

Solution 1. The balanced equation is given by

$$C_6H_5COOH_{(aq)} + \frac{15}{2}O_{2(g)} \to 7\,CO_{2(g)} + 3\,H_2O_{(\ell)}$$
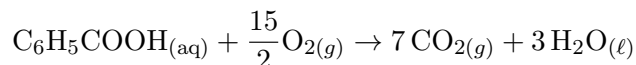
Given that $m = 1.24 \times 10^3$ g and $\Delta T = 3.45$ K, and since the process is isochoric, $q_{rxn} = \Delta U_{rxn}$, then

$$\Delta U = \Delta H - \Delta nRT = (-3228 \text{ kJ/mol}) - (-0.5 \text{ mol})(0.008314 \text{ kJ/mol K})(298 \text{ K}) = -3226.8 \text{ kJ/mol}$$

Then we need to find q_{rxn}.

$$q_{rxn} = n\Delta U_m = \frac{1.35 \text{ g}}{122 \text{ g/mol}} \times (-3226.8 \text{ kJ/mol}) = -35.72 \text{ kJ} = -q_{sur}$$

Thus,

$$q_{sur} = q_{H_2O} + q_{cal} = m_{H_2O}C_{H_2O}\Delta T + C_{cal}\Delta T = 35720 \text{ J}$$
$$(12.40 \text{ g})(4.184 \text{ J/g K})(3.45 \text{ K}) + (3.45 \text{ K})C_{cal} = 35720 \text{ J}$$
$$C_{cal} = \frac{(35720 \text{ J}) - (12.40 \text{ g})(4.184 \text{ J/g K})(3.45 \text{ K})}{3.45}$$
$$C_{cal} = 10301 \text{ J/K}$$

Question 2. *Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction*
$$C_6H_{12}O_6 \to 2\,CH_3CHOHCOOH$$

The standard enthalpy of formation $T = 298$ K for glucose and lactic acid are -1273.1 kJ/mol and -673.6 kJ/mol and the C_P are 219.2 J/mol K and 127.6 J/mol K respectively. Calculate the enthalpy of reaction when 5 g of glucose react at 330 K assuming the change in heat capacity of the reaction is negligible.

Solution 2. First, calculating ΔH_{rxn}

$$2(-673.6 \text{ kJ/mol}) - (-1273.1 \text{ kJ/mol}) = -74.1 \text{ kJ/mol} \qquad \text{(at 298 K)}$$

Then calculating ΔC_P,

$$\Delta C_P = 2(127.6 \text{ J/K}) - (219.2 \text{ J/K}) = 36 \text{ J/mol K}$$

Then at 330 K,

$$\Delta H_{330 \text{ K}} = \Delta H + \int_{298}^{330} C_P dT = (-74100 \text{ J/mol}) + (36 \text{ J/mol K})(330 - 298 \text{ K}) = -72978 \text{ J/mol}$$

Then for 5 g,

$$\Delta H = \frac{5}{180 \text{ g/mol}} = -2.03 \text{ kJ}$$

Substances	$\Delta_f H^\circ$ (J/mol K)	$C_{P,m}^\circ$ (J/mol K)
$CO_{(g)}$	-110.53	29.14
$H_2O_{(g)}$	-241.82	33.58
$CO_{2(g)}$	-393.51	37.11
$H_{2(g)}$		28.824

Question 3. *From standard enthalpies of formation and standard heat capacities available from the table below, calculate the enthalpies at 298 K and 398 K for the reaction.*

$$CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$$
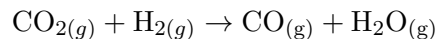
when 3 atm of $CO_{2(g)}$ reacts with an excess of $H_{2(g)}$ in a 1.0 L container at 298 K. Assume that the heat capacities are constant over the temperature range involved.

Solution 3. We have

$$\Delta H_{rxn}^\circ = \Delta H_f(CO) + \Delta H_f^\circ(H_2O) - \Delta H_f^\circ(O_2) - \Delta H_f^\circ(H_2)$$
$$= (-110.53)(-241.12) - (-393.5) = 41.2 \text{ kJ/mol}$$

Then

$$\Delta C_P = 29.14 + 33.58 - 37.11 - 28.824 = -3.214 \text{ J/mol K}$$

Lastly,

$$\Delta H_{rxn}^{398 \text{ K}} = 41160 \text{ J/mol} + \int_{298}^{398} (-3.214) \text{ J/mol K} dT = 40.84 \text{ kJ/mol}$$

for 0.123 mol, 5.02 kJ, as required.