⑦

The first law of thermodynamics:

$$U = Q + W$$

U — internal energy, Q — heat, W — work

reversibility:

a system is in equilibrium with its surrounding if an infinitesimal chang in the conditions in oposite directions results in opposite changes in its states

Heat changes:

$$dU = dQ + dW_{expan} + dW'$$

$$V = const, \quad W' = 0$$

$$\Delta U = Q_V \Rightarrow \boxed{c_V = \left.\frac{\partial U}{\partial T}\right|_V}$$ Heat capacity (at constant volume)

- c_V is a material property
- $c_V \to \infty \Rightarrow$ heat is absorbed, but no temperature change, latent heat is used for a phase transition e.g. melting of ice

Enthalpy $\boxed{H = U - pV}$

change in enthalpy is equal to the heat supplied at constant pressure $dH = dQ$
for $p = \text{const}$

$\Rightarrow$ Heat Capacity (at constant pressure) $\boxed{C_p = \frac{\partial H}{\partial T}\Big|_p}$

ideal gas:

$$H = U + pV = U + nRT$$

$$\Rightarrow \Delta H - \Delta U = \Delta n\, RT$$

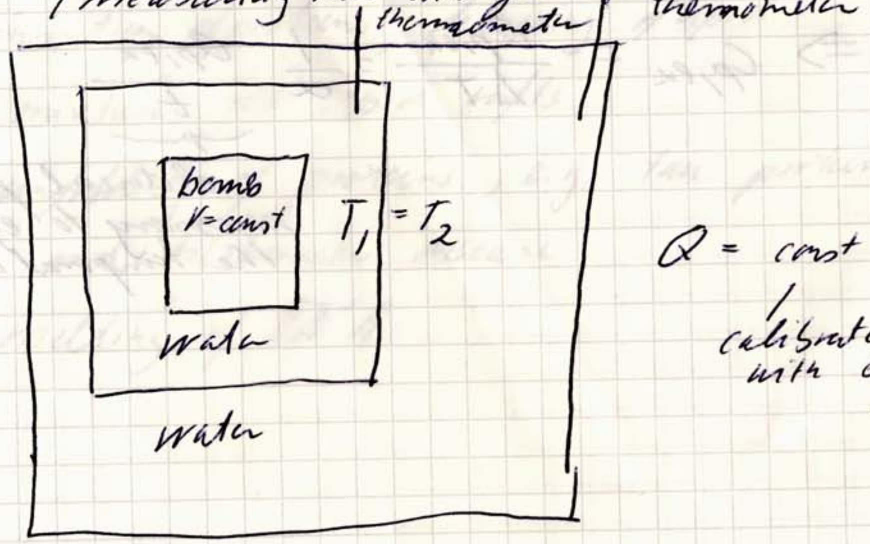
$$\Rightarrow \boxed{C_p - C_V = nR}$$

ideal $\quad C_{p,m} \approx a + bT + \frac{c}{T^2}$

Calorimetry

(measuring heat changes)

(i)

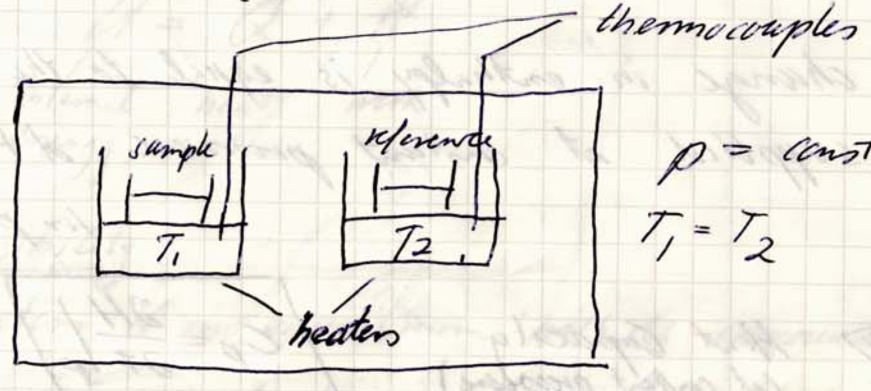


$Q = \text{const}\ \Delta T$

calibrate with electrical current

(9)

(ii) Differential Scanning Calorimeter (DSC)



p = const

$T_1 = T_2$

linear scan $T = T_0 + \alpha t$

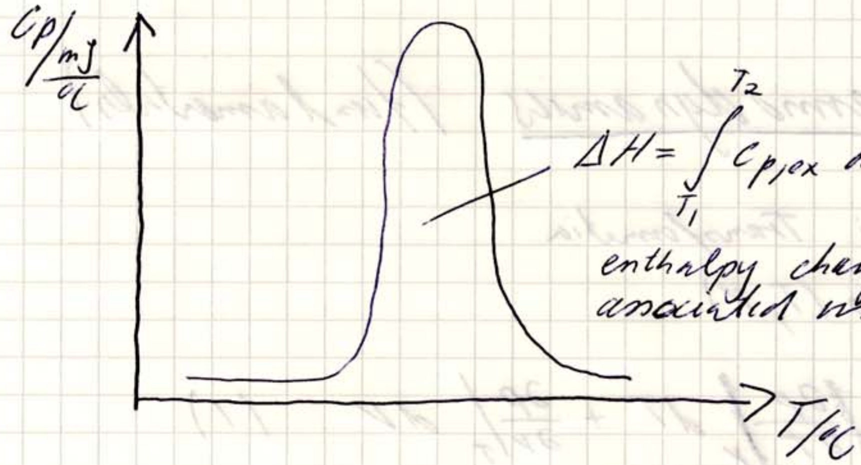
e.g. a endothermic process in the sample requires more heating in the sample to maintain $T_1 = T_2$

$$Q_p + Q_{p,ex} = (C_p + C_{p,ex})\,\Delta T$$

($Q_{p,ex}$ ↑ physical or chemical change in sample; $C_{p,ex}$ ↑ according change in heat capacity)

$$\Rightarrow C_{p,ex} = \frac{Q_{p,ex}}{\Delta T} = \frac{1}{\alpha}\,\frac{Q_{p,ex}}{t}$$

$\frac{Q_{p,ex}}{t}$ = electrical power necessary to equalize the temperature



$$\Delta H = \int_{T_1}^{T_2} C_{p,ex}\, dT$$

enthalpy changes associated with process

- determine the stability of proteins, nucleic acids and membranes
- large molecules attain complex 3-dimensional structures due to intra- and intermolecular interactions such as hydrogen bonding and hydrophobic interactions. Disruption of these interactions is an endothermic process that can be studied with a DSC
- phase changes in lipid membranes, insertion of proteins, demixing of lipid mixtures ⇒ lipid rafts
- unfolding of proteins, e.g. tau protein and Alzheimer disease
- melting of DNA

(11)

Thermodynamics (Fundamentals)

(i) Jacobi Transformation

$$p = p(T, V)$$

$$dp = \left.\frac{\partial p}{\partial T}\right|_V dT + \left.\frac{\partial p}{\partial V}\right|_T dV \qquad (1)$$

- differentials dT and dV in (1) are arbitary for given T, V. They determine the value of dp.

With the constraint $p = const$

$$\Rightarrow dp = 0$$

$$\Rightarrow \left.\frac{\partial V}{\partial T}\right|_p = - \frac{\left.\frac{\partial p}{\partial T}\right|_V}{\left.\frac{\partial p}{\partial V}\right|_T}$$