

59-240
Lecture 7
Enthalpy and Adiabatic Changes

$q = 0$
 $w < 0; \Delta U < 0$
 KE of molecules drop
 Thus, $\Delta T < 0$
 adiabatic expansion
 $V_f T_f^c = V_i T_i^c \quad c = \frac{C_{p,m}}{R}$
 Justification $T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$
 Justification $pV^\gamma = \text{constant}$
 $\gamma = \frac{C_{p,m}}{C_{v,m}}$

Adiabatic changes

If system changes volume, the internal energy is not equal to the heat supplied

The enthalpy describes the heat supplied for constant pressure processes

$H = U + pV$

$dH = dq \quad \Delta H = q_p$

Derivation: $dH = dq \quad \Delta H = q_p$

Enthalpy

heat capacity at constant pressure

$C_p = \left(\frac{\partial H}{\partial T} \right)_p$

$dH = C_p dT$

$q_p = C_p \Delta T$

extensive property

molar heat capacity, $C_{p,m}$ ($\text{J K}^{-1} \text{mol}^{-1}$)

specific heat capacity, $C_{p,m}^s$ ($\text{J K}^{-1} \text{g}^{-1}$)

intensive property

Heat capacity

Flame calorimeter Direct measure of ΔH

Bomb calorimeter Direct measure of ΔU

solids and liquids have very small molar volumes, so $H_m = U_m + pV_m \approx U_m$

Calorimeter comparison

$H = U + pV = U + nRT$

$\Delta H = \Delta U + \Delta n_{\text{gas}} RT$ in reactions where gas molecules are created or reacted (e.g., combustion)

Comparing H and U

constant p , most systems expand when heated, and do work on the surroundings while losing internal energy, with some energy supplied as heat leaking back into the surroundings

Variation of C_p with T
 $C_{p,m} = a + bT + \frac{c}{T^2}$

$C_p - C_v = nR$