

Calorimetry

is the science or act of measuring changes in state variables of a body for the purpose of deriving the heat transfer associated with changes of its state due, for example, to chemical reactions, physical changes, or phase transitions under specified constraints.

The amount of heat is calculated, when achieving the interaction within the calor of the equation:

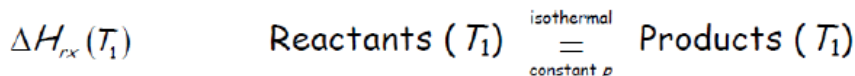
$$Q = mc\Delta t$$

Q: change in the amount of heat, m: Material mass in the surroundings, Δt : difference in temperature before and after interaction

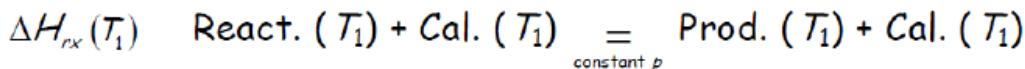
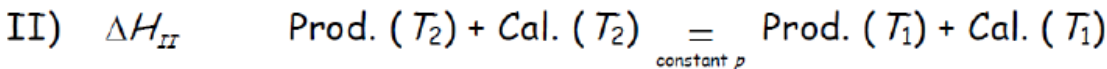
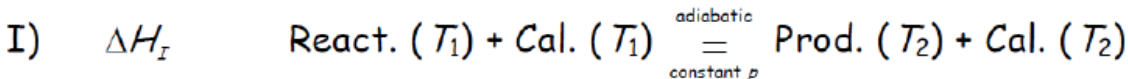
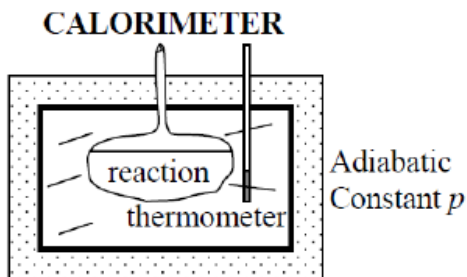
To calculate the molar enthalpy:

$$Q = n\Delta H$$

N: number of moles of the reactive substance



- Constant pressure (for solutions)



$$\Delta H_{rx}(T_1) = \Delta H_I + \Delta H_{II}$$

(I) Purpose is to measure $(T_2 - T_1)$

$$\text{Adiabatic, const. } p \Rightarrow q_p = 0 \Rightarrow \Delta H_I = 0$$

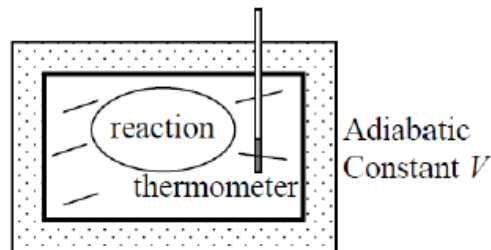
(II) Purpose is to measure heat q_p needed to take prod. + cal. from T_2 back to T_1 .

$$q_p = \int_{T_1}^{T_2} C_p (\text{Prod.} + \text{Cal.}) dT = \Delta H_{II}$$

$$\therefore \Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_p (\text{Prod.} + \text{Cal.}) dT \approx -\int_{T_1}^{T_2} C_p^{cal} dT = -C_p^{cal} \Delta T$$

- Constant volume (when gases involved)

CALORIMETER



$$\text{I) } \Delta U_I \quad \text{React. } (T_1) + \text{Cal. } (T_1) \stackrel{\text{adiabatic}}{=} \text{Prod. } (T_2) + \text{Cal. } (T_2)$$

$$\text{II) } \Delta U_{II} \quad \text{Prod. } (T_2) + \text{Cal. } (T_2) \stackrel{\text{constant } V}{=} \text{Prod. } (T_1) + \text{Cal. } (T_1)$$

$$\Delta U_{rx}(T_1) \quad \text{React. } (T_1) + \text{Cal. } (T_1) \stackrel{\text{constant } V}{=} \text{Prod. } (T_1) + \text{Cal. } (T_1)$$

$$\Delta U_{rx}(T_1) = \Delta U_I + \Delta U_{II}$$

(I) Purpose is to measure ($T_2 - T_1$)

$$\text{Adiabatic, const. } V \Rightarrow q_V = 0 \Rightarrow \Delta U_T = 0$$

(II) Purpose is to measure heat q_V needed to take prod. + cal. from T_2 back to T_1 .

$$q_V = \int_{T_1}^{T_2} C_V (\text{Prod.} + \text{Cal.}) dT = \Delta U_{IT}$$

$$\therefore \Delta U_{rx}(T_1) = -\int_{T_1}^{T_2} C_V (\text{Prod.} + \text{Cal.}) dT \approx -\int_{T_1}^{T_2} C_V^{cal} dT = -C_V^{cal} \Delta T$$

Now use $H = U + pV$ or $\Delta H = \Delta U + \Delta(pV)$

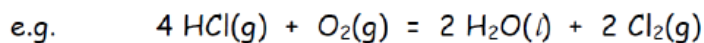
$$\text{Ideal gas} \Rightarrow \Delta(pV) = R\Delta(nT)$$

$$\text{Isothermal } T = T_1 \Rightarrow \Delta(pV) = RT_1 \Delta n_{gas}$$

$$\therefore \Delta H_{rx}(T_1) = \Delta U_{rx}(T_1) + RT_1 \Delta n_{gas}$$

$$\Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_V (\text{Prod.} + \text{Cal.}) dT + RT_1 \Delta n_{gas} \approx -C_V^{cal} \Delta T + RT_1 \Delta n_{gas}$$

Difference between ΔU and ΔH small but measurable



$$T_1 = 298.15 \text{ K}$$

$$\Delta U_{rx}(T_1) = -195.0 \text{ kJ} \quad \Delta n_{gas} = -3 \text{ moles}$$

$$\begin{aligned} \Delta H_{rx}(T_1) &= -195.0 \text{ kJ} + (-3 \text{ mol})(298.15 \text{ K})(8.314 \times 10^{-3} \text{ kJ/K-mol}) \\ &= -202.43 \text{ kJ} \end{aligned}$$

Note:

Calorimeter thermal mass \gg product thermal mass

EX/A calorimeter is to be calibrated: (72.55 g) of water at (71.6 °C) added to a calorimeter containin (58.85g) of water at (22.4 °C). After stirring and waiting for the system to equilibrate, the final temperature reached (47.3 °C). Calculate the heat capacity of the calorimeter. (The specific heat capacity of water is $4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$).

Sol/

1) Energy lost by the hot water:

$$q = m C_p \Delta T$$

$$q = (72.55 \text{ g}) (4.184 \text{ J/g}^{-1} \text{ }^\circ\text{C}^{-1}) (24.3 \text{ }^\circ\text{C})$$

$$q = 7376.24 \text{ J}$$

2) Energy gained by the cold water:

$$q = m C_p \Delta T$$

$$q = (58.85 \text{ g}) (4.184 \text{ J/g}^{-1} \text{ }^\circ\text{C}^{-1}) (24.9 \text{ }^\circ\text{C})$$

$$q = 5818.54 \text{ J}$$

3) The calorimeter got the rest:

$$7376.24 - 5818.54 = 1557.7 \text{ J}$$

4) Heat capacity of the calorimeter:

$$q = C \Delta T$$

$$C = q / \Delta T$$

$$1557.7 \text{ J} / 24.9 \text{ }^\circ\text{C} = 62.558 \text{ J/}^\circ\text{C} \text{ (round off as you see fit)}$$

EX/ A student wishes to determine the heat capacity of a coffee-cup calorimeter. After mixing 100.0 g of water at 58.5 °C with 100.0 g of water, already in the calorimeter, at 22.8 °C, the final temperature of the water is 39.7 °C. Calculate the heat capacity of the calorimeter in J/°C. (Use $C_p = 4.184$ J/g °C as the specific heat of water.) ?

EX/A 43.2 g block of an unknown metal at 89.0 °C was dropped into an insulated vessel containing 43.00 g of ice and 26.00 g of water at 0 °C. After the system had reached equilibrium it was determined that 9.15 g of the ice had melted. What is the specific heat of the metal? (The heat of fusion of ice = 334.166 J g⁻¹.) ?

EX/ If you know that ΔU of ethylene C_2H_4 at (17°C), , when the volume is constant equals (-332.19 kcal), calculate ΔH at constant pressure ($\Delta n = -2$), ($R = 1.98$ cal.K⁻¹.mol⁻¹) ?