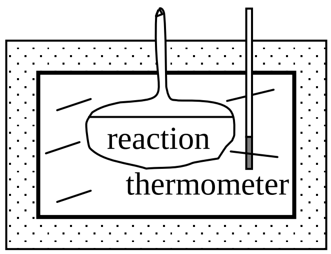
5.60 Thermodynamics & Kinetics
Spring 2008

Calorimetry

The objective is to measure

$\Delta H_{rx}(T_1)$ Reactants (T_1) $\underset{\text{constant } p}{\overset{\text{isothermal}}{=}}$ Products (T_1)

- <u>Constant pressure</u> (for solutions)



I) ΔH_I React. (T_1) + Cal. (T_1) $\underset{\text{constant } p}{\overset{\text{adiabatic}}{=}}$ Prod. (T_2) + Cal. (T_2)

II) ΔH_{II} Prod. (T_2) + Cal. (T_2) $\underset{\text{constant } p}{=}$ Prod. (T_1) + Cal. (T_1)

$\Delta H_{rx}(T_1)$ React. (T_1) + Cal. (T_1) $\underset{\text{constant } p}{=}$ Prod. (T_1) + Cal. (T_1)

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

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

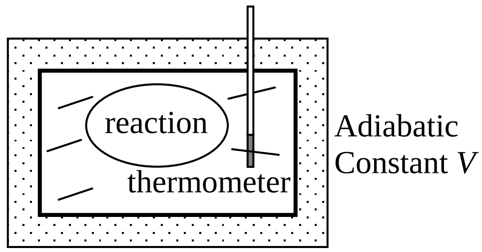
Adiabatic, const. p $\Rightarrow$ $q_p = 0$ $\Rightarrow$ $\Delta H_I = 0$

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

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

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

• <u>Constant volume</u> (when gases involved)



I) ΔU_I React. (T_1) + Cal. (T_1) $\underset{\text{constant } V}{\overset{\text{adiabatic}}{=}}$ Prod. (T_2) + Cal. (T_2)

II) ΔU_{II} Prod. (T_2) + Cal. (T_2) $\underset{\text{constant } V}{=}$ Prod. (T_1) + Cal. (T_1)

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

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

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

Adiabatic, const. V $\Rightarrow$ $q_V = 0$ $\Rightarrow$ $\Delta U_I = 0$

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

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

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

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

Assume only significant contribution to $\Delta(pV)$ is from gases.

Ideal gas $\Rightarrow \quad \Delta(pV) = R\Delta(nT)$

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

$$\therefore \quad \boxed{\begin{array}{l} \Delta H_{rx}(T_1) = \Delta U_{rx}(T_1) + RT_1\Delta n_{gas} \\ \\ \Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_V(Prod. + Cal.)dT + RT_1\Delta n_{gas} \approx -C_V^{cal}\Delta T + RT_1\Delta n_{gas} \end{array}}$$

Difference between ΔU and ΔH small but measurable

e.g. $4\ HCl(g) + O_2(g) = 2\ H_2O(l) + 2\ Cl_2(g)$

$T_1 = 298.15$ K

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

$\Delta H_{rx}(T_1) = -195.0\ \text{kJ} + (-3\ \text{mol})(298.15\ \text{K})(8.314\times10^{-3}\ \text{kJ/K-mol})$
$= -202.43$ kJ

Now let's imagine really running this reaction in a constant-V calorimeter with $C_v = 10$ kJ/K

Calorimeter thermal mass >> product thermal mass
Heat goes to changing calorimeter T
Often no need to know product C_p or C_V value

Bond energies: An approximate method for estimating ΔH_f°

Really bond enthalpies, but usually $\Delta(pV)$ << difference

1) Measure bond energies for known compounds
2) Use them to estimate ΔH_f° for unknown compounds

e.g.

$CH_4(g) = C(\text{graphite}) + 2\,H_2(g) \qquad \Delta H_I = -\Delta H^\circ_{f,CH_4}$

$C(\text{graphite}) = C(g) \qquad \Delta \bar{H}_C\ (\text{atomization})$

$2\,H_2(g) = 4\,H(g) \qquad 2\Delta \bar{H}_{H_2}\ (\text{atomization})$

$CH_4(g) = C(g) + 4\,H(g) \qquad \Delta H$

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   H
   |
H- C -H
   |
   H
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$\Delta H = 4B_{C\text{-}H} \qquad B_{C\text{-}H} = 416.2\ \text{kJ}$

$$4\,B_{C\text{-}H} = -\Delta H^\circ_{f,CH_4} + \Delta \bar{H}_{C(atom.)} + 2\Delta \bar{H}_{H_2(atom.)} \Rightarrow \boxed{B_{C-H} = 416.2\ \text{kJ}}$$

$C_2H_6(g) = C(g) + 6\,H(g)$

```
   H  H
   |  |
H- C- C -H
   |  |
   H  H
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$$\Delta H = B_{C\text{-}C} + 6B_{C\text{-}H}$$
$$= -\Delta H^\circ_{f,C_2H_6} + 2\Delta \bar{H}_{C(atom.)} + 3\Delta \bar{H}_{H_2(atom.)} \Rightarrow \boxed{B_{C-C} = 342\ \text{kJ}}$$

Now estimate ΔH_f° for n-pentane, C_5H_{12} $\quad CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

$5\,C(\text{graphite}) = 5\,C(g) \qquad 5\Delta \bar{H}_{C(atom.)}$

$6\,H_2(g) = 12\,H(g) \qquad 6\Delta \bar{H}_{H_2(atom.)}$

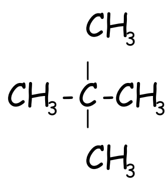
$5\,C(g) + 12\,H(g) = C_5H_{12}(g) \qquad \Delta H \approx -\left(4B_{C-C} + 12B_{C-H}\right)$

$5\,C(\text{graphite}) + 6\,H_2(g) = C_5H_{12}(g) \qquad \Delta H^\circ_{f,C_5H_{12}}$

$$\Delta H^{o}_{f,C_5H_{12}} \approx -\left(4B_{C-C} + 12B_{C-H}\right) + 5\Delta \overline{H}_{C(atom.)} + 6\Delta \overline{H}_{H_2(atom.)}$$

~ <u>-152.6 kJ</u> (estimated)

Actual $\Delta H^{\circ}_{f,C_5H_{12}}$ (n-pentane) = <u>-146.4 kJ</u>

But 

is also C_5H_{12} with 4 C-C bonds, 12 C-H bonds

$\Rightarrow$ $\Delta H^{\circ}_{f,C_5H_{12}}$ ~ <u>-152.6 kJ</u> (estimated using bond energies)

Actual $\Delta H^{\circ}_{f,C_5H_{12}}$ (neopentane) = <u>-166.1 kJ</u>