STATISTICAL MOLECULAR THERMODYNAMICS

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Video 5.7

Enthalpy

CONSTANT PRESSURE CONDITIONS

For a *reversible* process where the work is restricted to pressure-volume work:

$$\Delta U = q + w = q - \int_{V_1}^{V_2} P\,dV$$

- At *constant volume* $V_1=V_2$: $\quad \Delta U = q_V$

constant volume

ΔU is the heat at *constant volume* (can be measured using bomb calorimetry)

- However, in chemistry it is often more convenient to work at *constant pressure*, for which the heat is,

$$q_P = \Delta U + P_{\text{ext}}\int_{V_1}^{V_2} dV = \Delta U + P\Delta V$$

So q_P is not equal to ΔU.

constant pressure (not a function of V)

ENTHALPY: A STATE FUNCTION

At *constant volume*, $q_V = \Delta U$; q_V is a state function

At *constant pressure*, $q_P = \Delta U + P\Delta V$ is also a state function

Define the *enthalpy*: $H = U + PV$ (general)

$dH = dU + PdV + VdP$ (general)

At *constant pressure*: $\Delta H = \Delta U + P\Delta V$

confirming that the more general enthalpy *is* equal to the heat at *constant pressure*, $\Delta H = q_P$

H has the same role at constant P that U has at constant V

ENTHALPY VS INTERNAL ENERGY

Ice (H_2O) melting at 273 K and one atm, q_P = 6.01 kJ•mol^{-1}, so

$$\Delta\overline{H} = q_P = 6.01\,\text{kJ} \bullet \text{mol}^{-1}$$

273 K molar volumes are

$$\left.\begin{aligned} \text{solid: } \overline{V}_s &= 0.0196\,\text{L} \bullet \text{mol}^{-1} \\ \text{liquid: } \overline{V}_l &= 0.0180\,\text{L} \bullet \text{mol}^{-1} \end{aligned}\right\}$$

rare and important!

What is $\Delta\overline{U}$? $\quad \Delta\overline{U} = \Delta\overline{H} - P\Delta\overline{V}$ (at constant pressure)

$$\Delta\overline{U} = \left(6.01\,\text{kJ} \bullet \text{mol}^{-1}\right) - \left(1\,\text{atm}\right)\left(0.0180\,\text{L} \bullet \text{mol}^{-1} - 0.0196\,\text{L} \bullet \text{mol}^{-1}\right)$$

$$\Delta\overline{U} = \left(6.01\,\text{kJ} \bullet \text{mol}^{-1}\right) + \left(1.60 \times 10^{-3}\,\text{L} \bullet \text{atm} \bullet \text{mol}^{-1}\right)\left(\frac{0.008314\,\text{kJ}}{0.08206\,\text{L} \bullet \text{atm}}\right) \approx 6.01\,\text{kJ} \bullet \text{mol}^{-1}$$

$$\Delta\overline{U} \approx 6.01\,\text{kJ} \bullet \text{mol}^{-1}$$

Because ΔV is *very* small, $P\Delta V$ is also very small, and so there is neglibgible difference between ΔH and ΔU

ENTHALPY VS INTERNAL ENERGY

Water (H_2O) boiling at 373 K and one atm, q_P = 40.7 kJ•mol^{-1}, so

$$\Delta\overline{H} = q_P = 40.7\ \text{kJ} \bullet \text{mol}^{-1}$$

373 K molar volumes are gas: $\overline{V}_g = 30.6\ \text{L} \bullet \text{mol}^{-1}$

liquid: $\overline{V}_l = 0.0180\ \text{L} \bullet \text{mol}^{-1}$

What is $\Delta\overline{U}$? $\Delta\overline{U} = \Delta\overline{H} - P\Delta\overline{V}$ (at constant pressure)

$$\Delta\overline{U} = \left(40.7\ \text{kJ} \bullet \text{mol}^{-1}\right) - \left(1\ \text{atm}\right)\left(30.6\ \text{L} \bullet \text{mol}^{-1} - 0.0180\ \text{L} \bullet \text{mol}^{-1}\right)$$

$$\Delta\overline{U} = \left(40.7\ \text{kJ} \bullet \text{mol}^{-1}\right) - \left(30.58\ \text{L} \bullet \text{atm} \bullet \text{mol}^{-1}\right)\left(\frac{0.008314\ \text{kJ}}{0.08206\ \text{L} \bullet \text{atm}}\right) = 37.6\ \text{kJ} \bullet \text{mol}^{-1}$$

$$\Delta\overline{U} = 37.6\ \text{kJ} \bullet \text{mol}^{-1}$$

The ΔU term relates to the energy to overcome *intermolecular forces* in the liquid, the ΔH term is *larger* as it includes the $P\Delta V$ expansion work on going from liquid to vapor