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:

\[ \Delta U = q + w = q - \int_{V_1}^{V_2} PdV \]

- At constant volume \( V_1 = V_2 \): \( \Delta U = q_V \)
  \( \Delta U \) 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 \( \Delta U \).
**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)

\[
dH = dU + PdV + VdP \quad \text{(general)}
\]

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 (H₂O) melting at 273 K and one atm, \( q_P = 6.01 \text{ kJ} \cdot \text{mol}^{-1} \), so

\[
\Delta H = q_P = 6.01 \text{ kJ} \cdot \text{mol}^{-1}
\]

273 K molar volumes are

- solid: \( \bar{V}_s = 0.0196 \text{ L} \cdot \text{mol}^{-1} \)
- liquid: \( \bar{V}_l = 0.0180 \text{ L} \cdot \text{mol}^{-1} \)

What is \( \Delta U \)?

\[
\Delta U = \Delta H - P\Delta V
\]

(at constant pressure)

\[
\Delta U = \left( 6.01 \text{ kJ} \cdot \text{mol}^{-1} \right) - \left( 1 \text{ atm} \right) \left( 0.0180 \text{ L} \cdot \text{mol}^{-1} - 0.0196 \text{ L} \cdot \text{mol}^{-1} \right)
\]

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

\[
\Delta U \approx 6.01 \text{ kJ} \cdot \text{mol}^{-1}
\]

Because \( \Delta V \) is very small, \( P\Delta V \) is also very small, and so there is negligible difference between \( \Delta H \) and \( \Delta U \)
Enthalpy vs Internal Energy

Water (H₂O) boiling at 373 K and one atm, \( q_P = 40.7 \text{ kJ} \cdot \text{mol}^{-1} \), so

\[
\Delta \overline{H} = q_P = 40.7 \text{ kJ} \cdot \text{mol}^{-1}
\]

373 K molar volumes are
- gas: \( \overline{V}_g = 30.6 \text{ L} \cdot \text{mol}^{-1} \)
- liquid: \( \overline{V}_l = 0.0180 \text{ L} \cdot \text{mol}^{-1} \)

What is \( \Delta \overline{U} \)?

\[
\Delta \overline{U} = \Delta \overline{H} - P \Delta \overline{V}
\]

(at constant pressure)

\[
\Delta \overline{U} = (40.7 \text{ kJ} \cdot \text{mol}^{-1}) - (1 \text{ atm}) (30.6 \text{ L} \cdot \text{mol}^{-1} - 0.0180 \text{ L} \cdot \text{mol}^{-1})
\]

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

\[
\Delta \overline{U} = 37.6 \text{ kJ} \cdot \text{mol}^{-1}
\]

The \( \Delta U \) term relates to the energy to overcome intermolecular forces in the liquid, the \( \Delta H \) term is larger as it includes the \( P \Delta V \) expansion work on going from liquid to vapor.