Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 6.1

Entropy
Spontaneity — Why?

Consider throwing a chunk of potassium in the Mississippi river.

\[ \text{K} + \text{H}_2\text{O} \rightarrow \text{KOH} + \frac{1}{2} \text{H}_2 \]

Consider bubbling hydrogen through a solution of KOH. What happens?

Why does it go the direction it does? Is it exothermicity?
\( \Delta H = 0 \) but **Spontaneous**

Insulated system (so \( \delta q = 0 \))

\( P_{\text{ext}} \) is zero (so \( \delta w = 0 \))

\( \Delta U = \delta q + \delta w = 0 \)

For an ideal gas, if \( \Delta U = 0 \) then \( \Delta T = 0 \)

\( \Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = \Delta U + nR\Delta T = 0 \)

*but it only ever goes one way…*
\[ \Delta H = 0 \text{ but Spontaneous} \]

Insulated system (so \( \delta q = 0 \))

\( \Delta V \) is zero (so \( \delta w = 0 \))

\( \Delta U = \delta q + \delta w = 0 \)

For ideal gases, if \( \Delta U = 0 \) then \( \Delta T = 0 \)

\[ \Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = \Delta U + nR\Delta T = 0 \]

*but it only ever goes one way…*
Disorder as a Driving Force?

Examples of spontaneous processes that are either thermo-neutral ($\Delta H = 0$) or endothermic ($\Delta H > 0$) have in common an increase in the disorder or randomness of the system, e.g., the mixing of Br$_2$ and N$_2$ across vessels.

Hypothesis: Systems spontaneously evolve to increase their disorder

There is an interplay between changing the energy of the system and increasing its disorder that determines the direction of a spontaneous process. To explore this further, consider the heat transfer associated with a small reversible change in the temperature and volume of an ideal gas:

$$\delta q_{rev} = dU - \delta w_{rev} = C_v(T)\,dT + \frac{nRT}{V} \,dV$$

commingling of variables renders differential inexact
A New State Function: Entropy

If we divide both sides of $\delta q_{\text{rev}}$ equation by $T$ to eliminate $T$ from last term:

$$\frac{\delta q_{\text{rev}}}{T} = \frac{C_v(T)}{T} dT + \frac{nR}{V} dV$$

The quantity on the left-hand side of the equation is now an exact differential

$$\frac{C_v(T)}{T} dT + \frac{nR}{V} dV = d\left[ \int \frac{C_v(T)}{T} dT + nR \int \frac{1}{V} dV + \text{constant} \right]$$

Thus, $\frac{\delta q_{\text{rev}}}{T}$ is a state function and it is called *entropy* ($S$).

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

Greek: “internal transformation”