STATISTICAL MOLECULAR THERMODYNAMICS

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Video 8.1

Helmholtz Free Energy

SPONTANEITY REDUX

$$dS \geq 0$$ is the condition for spontaneity only for an *isolated* system (constant U and V)

If the system is *not* isolated then we must consider the entropy of *both* the system *and* the surroundings to evaluate the *total* change ΔS_{total}, which is not very convenient.

Consider a system at constant T and V. The system is not isolated since heat *can* flow to maintain constant T. As a result $dS \geq 0$ for the system alone is *not* the criterion for a spontaneous process.

So, what *is* the criterion for a spontaneous process at constant T and V?
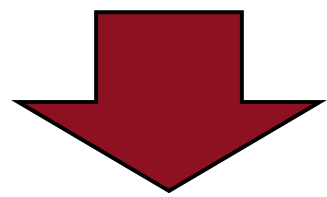
SPONTANEITY AT CONSTANT T AND V

From the second law:

$$dS \geq \frac{\delta q}{T} \rightarrow \delta q \leq TdS$$

At constant V:

$$\delta w = -P_{ext}dV = 0$$

The first law: $dU = \delta q + \delta w$

$$dU \underset{\text{reversible}}{\overset{\text{irreversible}}{\leq}} TdS \quad \text{(constant } V\text{)}$$

Note that for an isolated system $dU = 0$ and we recover $dS \geq 0$

THE HELMHOLTZ FREE ENERGY

Hermann von Helmholtz

$$dU \leq TdS \longrightarrow dU - TdS \leq 0$$

(constant V)

irreversible

$$d(U - TS) \leq 0 \quad \text{(constant } T \text{ and } V\text{)}$$

reversible

Define a new *state function*, the **Helmholtz free energy**, A:

$$A = U - TS$$

spontaneous

(constant T and V) $\quad dA \leq 0$

at equilibrium
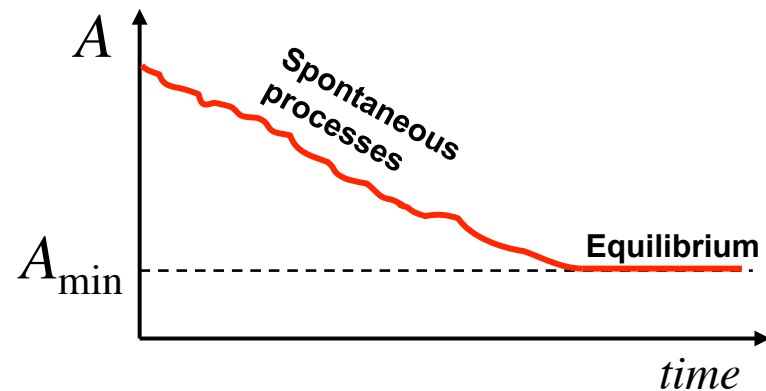
Helmholtz

Hermann von Helmholtz

"Whoever, in the pursuit of science, seeks after immediate practical utility, may generally rest assured that he will seek in vain."

(inventor of the opthalmoscope)

Physician and professor of physiology and psychology who did fundamental work on the transmission of nerve signals, opthalmology, auditory perception, oh, and thermodynamics…

DEUTSCHE BUNDESPOST HERMANN VON HELMHOLTZ 1821 - 1894

100

1994

Academic appointments at Königsberg, Bonn, Heidelberg, and, ultimately, as Professor of Physics at Berlin, where he was a senior colleague of Max Planck

THE HELMHOLTZ FREE ENERGY

$$A = U - TS \qquad \text{(definition)}$$

$$\Delta A = \Delta U - T\Delta S \qquad \text{(isothermal change)}$$

spontaneous

$$dA \leq 0 \longrightarrow \Delta A = \Delta U - T\Delta S \leq 0 \quad \text{(constant } T \text{ and } V\text{)}$$

at equilibrium

- For a process to take place spontaneously there is a compromise between lowering the energy and increasing the entropy. Entropy becomes more important at high T.

- A process where ΔA is positive *will not take place spontaneously* at constant T and V. In order for such a process to take place you must add something such as work.

ISOTHERMAL WORK FROM A SPONTANEOUS PROCESS

$$\Delta A = \Delta U - T\Delta S$$

A is a state function, so to evaluate it we can take a *reversible* path from one state to another $\Longrightarrow$ $\Delta S = \dfrac{q_{rev}}{T}$ $\rightarrow$ $T\Delta S = q_{rev}$

$$\Delta A = \Delta U - q_{rev}$$

$$\boxed{\Delta A = w_{rev}}$$ *(isothermal, reversible)*

- For $\Delta A < 0$, the process is spontaneous and w_{rev} is the *maximum* (free) work (*Arbeit*) that can be extracted ($-w_{rev} > -w_{irr}$).

- For $\Delta A > 0$, the process is *not* spontaneous and w_{rev} is the *minimum* work that must be done to drive the process.