STATISTICAL MOLECULAR THERMODYNAMICS

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Video 6.1
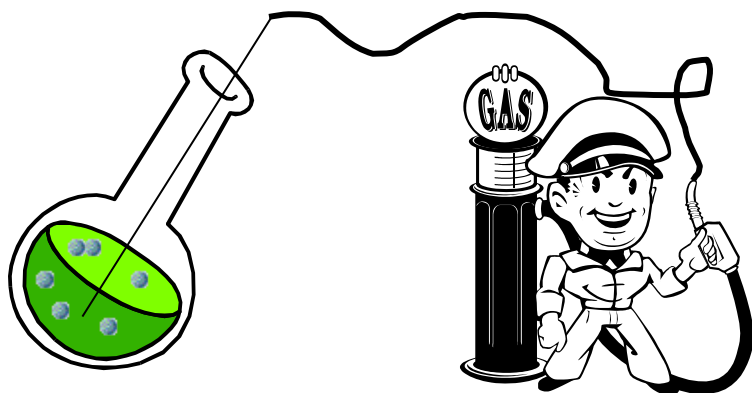
Entropy

SPONTANEITY — WHY?

Consider throwing a chunk of potassium in the Mississippi river.

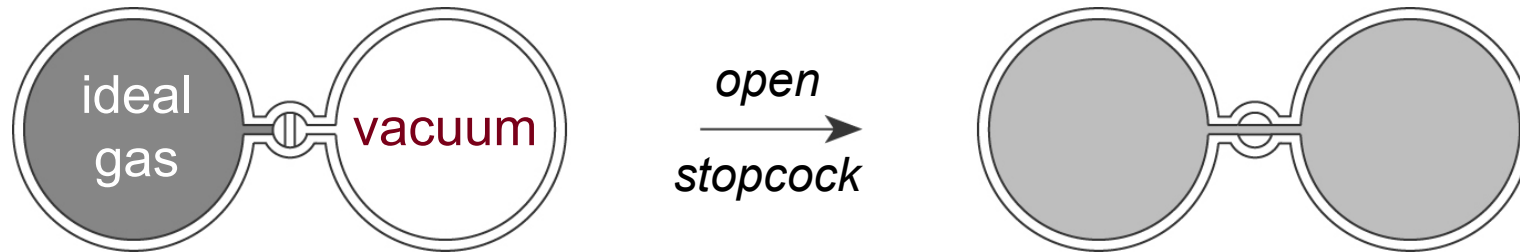$$K + H_2O \longrightarrow \text{(explosion)} \longrightarrow KOH + \tfrac{1}{2}H_2$$

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_{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…

$\Delta H = 0$ BUT SPONTANEOUS

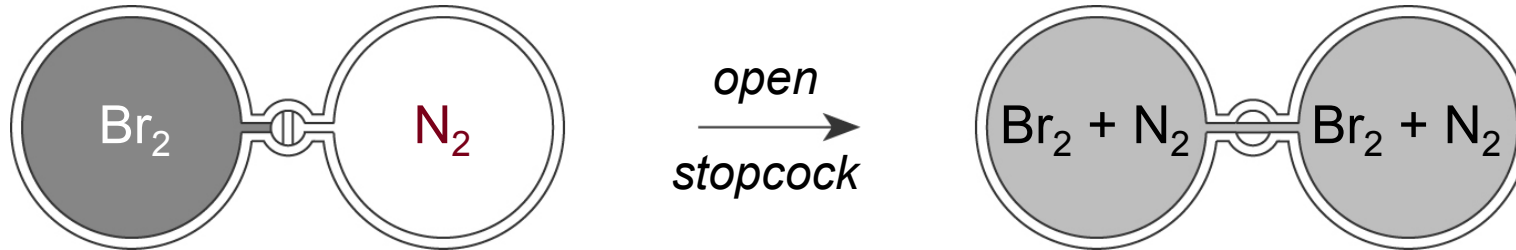Insulated system (so $\delta q = 0$)

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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*:

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

commingling of variables renders differential inexact

A New State Function: Entropy

If we divide both sides of δq_{rev} equation by T to eliminate T from last term:

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

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

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

Greek: "internal transformation"