

STATISTICAL MOLECULAR THERMODYNAMICS

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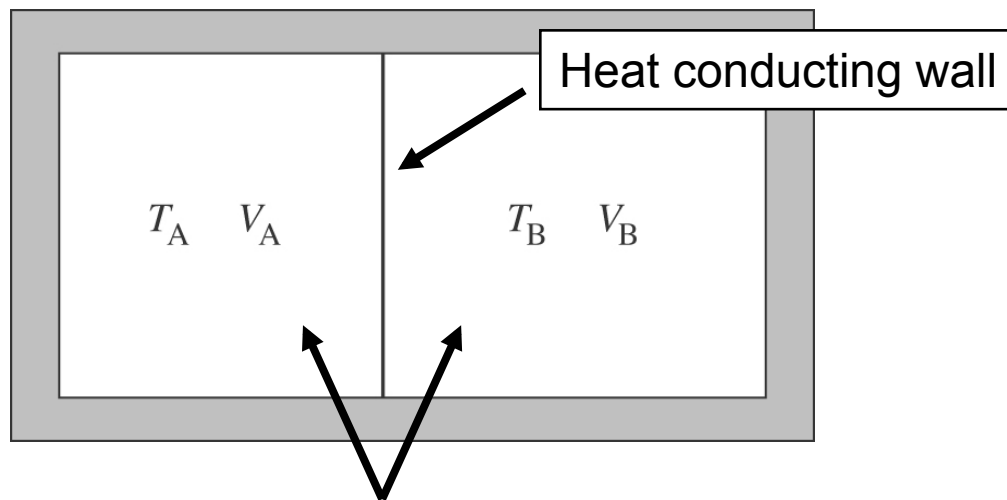
Video 6.3

Spontaneity and the Second Law

HEAT FLOW IN A SPECIAL SYSTEM

Energy as heat flows spontaneously from a region of higher temperature to a region of lower temperature (sometimes called The Zeroth Law of Thermodynamics)

Consider an *isolated, rigid* two compartment system



$$U_A + U_B = \text{constant}$$

$$V_A = \text{constant}$$

$$V_B = \text{constant}$$

$$S = S_A + S_B$$

Ideal gases in equilibrium, but not with each other when brought into contact

Isolated, rigid: No exchange of energy with surroundings, no work

DETERMINATION OF ENERGY AND ENTROPY

$$dV_A = dV_B = 0 \quad \rightarrow \quad \left. \begin{aligned} dU_A &= \delta q_{rev} = T_A dS_A \\ dU_B &= \delta q_{rev} = T_B dS_B \end{aligned} \right\} \text{No work}$$

$$dS = dS_A + dS_B = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} \quad dU_A = -dU_B$$

consequence of $U_A + U_B = \text{constant}$

$$dS = dU_B \left(\frac{1}{T_B} - \frac{1}{T_A} \right)$$

$T_B > T_A$	$dU_B < 0$	$dS > 0$
$T_A > T_B$	$dU_B > 0$	$dS > 0$
$T_A = T_B$	$dU_B = 0$	$dS = 0$

SPONTANEITY AND ENTROPY

The spontaneous flow of energy as heat from a body at a higher temperature to a body at a lower temperature is governed by the condition $dS > 0$.

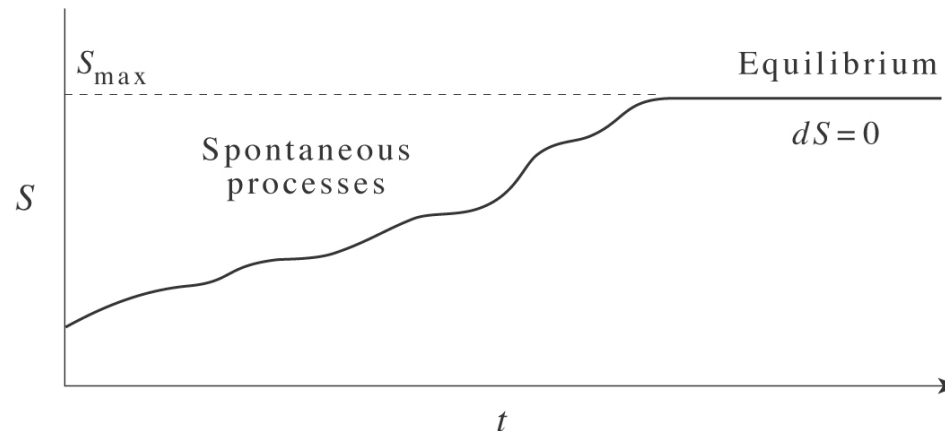
In an isolated system, the energy remains constant, so any spontaneous process must be due to an increase in entropy. Unlike energy, *entropy is not conserved*; it increases whenever a spontaneous process takes place. The entropy of an isolated system will continue to increase until the system is in equilibrium. An isolated system at equilibrium will have *maximal entropy*.

$dS > 0$ (spontaneous process in an isolated system)

$dS = 0$ (reversible process in an isolated system)

CONNECTING TO SURROUNDINGS

Isolated system:



What about a general situation (non-isolated system)? The change in entropy (dS) comes from two “sources”: the entropy *produced* by an irreversible process itself and the entropy due to the energy as heat *exchanged* between the system and the surroundings.

entropy produced
(always non-negative)

exchange entropy (could be + or - or 0)

$$dS = dS_{\text{prod}} + dS_{\text{exch}} = dS_{\text{prod}} + \frac{\delta q}{T}$$

THE SECOND LAW

Reversible:

$$dS = 0 + \frac{\delta q_{rev}}{T} = \frac{\delta q_{rev}}{T}$$

$$dS = dS_{prod} + \frac{\delta q}{T}$$

Irreversible:

$$dS = dS_{prod} + \frac{\delta q_{irr}}{T} > \frac{\delta q_{irr}}{T}$$

There is a thermodynamic function of a system called the entropy, S , such that for any change in the thermodynamic state of the system,

$$dS \geq \frac{\delta q}{T} \qquad \Delta S \geq \int \frac{\delta q}{T}$$

where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage

ENTROPY OF IRREVERSIBLE PROCESS

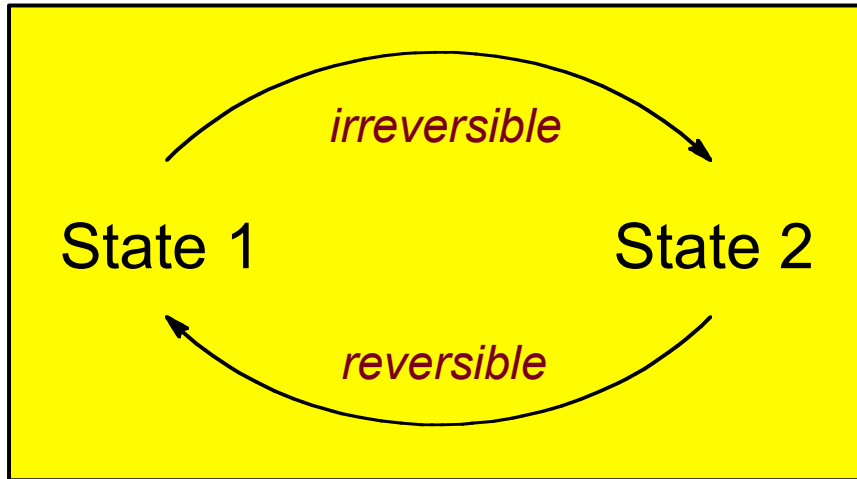
$$\Delta S \geq \int \frac{\delta q}{T}$$

$$\Delta S_{1 \rightarrow 2 \rightarrow 1} = \oint dS = 0$$

because entropy is a state function

$$\Delta S > \int_1^2 \frac{\delta q_{irr}}{T} + \int_2^1 \frac{\delta q_{rev}}{T}$$

because some step is irreversible



system isolated during irreversible step, placed back in contact with surroundings for reversible step

$$0 > 0 + \underbrace{S_1 - S_2}_{\text{by definition}}$$

system isolated



$$S_2 > S_1$$

an irreversible process always increases entropy

RESTATEMENT OF LAWS 1 AND 2



The energy of the Universe is constant;
the entropy is tending to a maximum

Rudolph Clausius (Entropy, 1865)

$$\Delta U = q + w \qquad \Delta S \geq \int \frac{\delta q}{T}$$