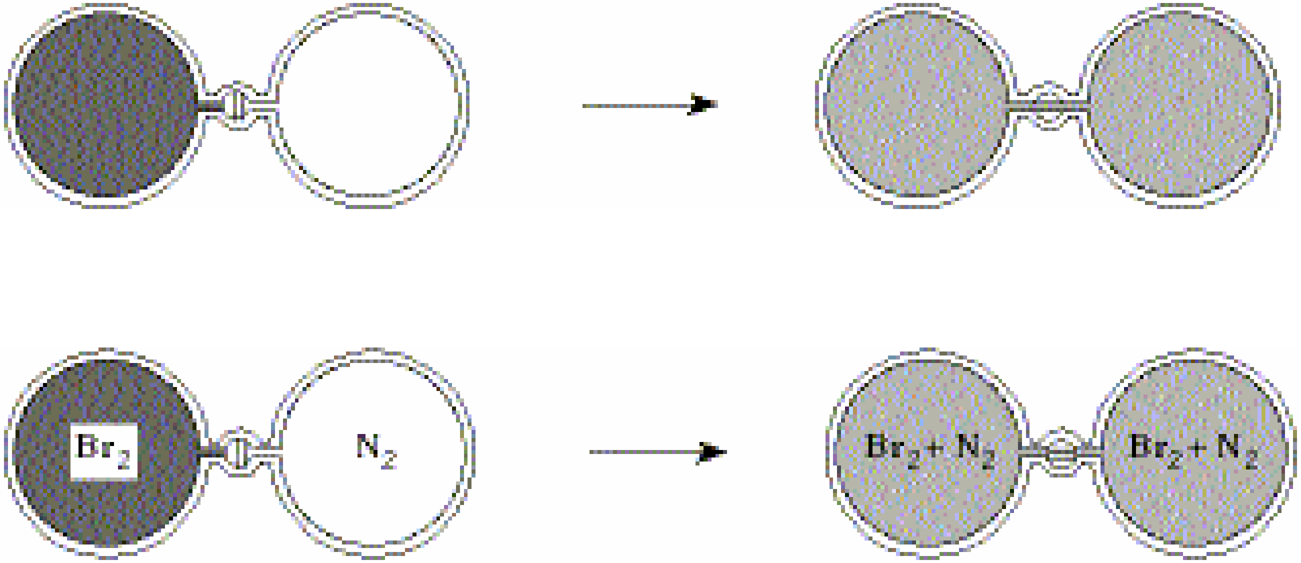
Spontaneous “Reactions”?

At one time scientists thought that for a reaction (or process) to be spontaneous, it must be exothermic (evolve energy)… like a ball rolling down a hill.

Let’s do a thought experiment to test this hypothesis…



$Ba(OH)_2$ (s) + 2 NH_4NO_3 (s) → $Ba(NO_3)_2$ (s) + 2 H_2O (l) + 2 NH_3 (aq)

These spontaneous reactions (processes) can’t be explained by 1st Law alone!

What's missing?

Examples where the processes are either thermoneutral ($\Delta H = 0$) or endothermic have in common an ***increase in the disorder*** or randomness of the system.

There is a ***competition*** between the tendency to minimize the energy and maximize the disorder.

We know how to calculate and consider the energy. How do we quantify the disorder?

We need a ***state function*** that describes disorder. We rule out heat because it is a path function…

A new state function

Consider the heat transfer associated with small reversible change in T and V of an ideal gas:

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

We know q is not a state function…

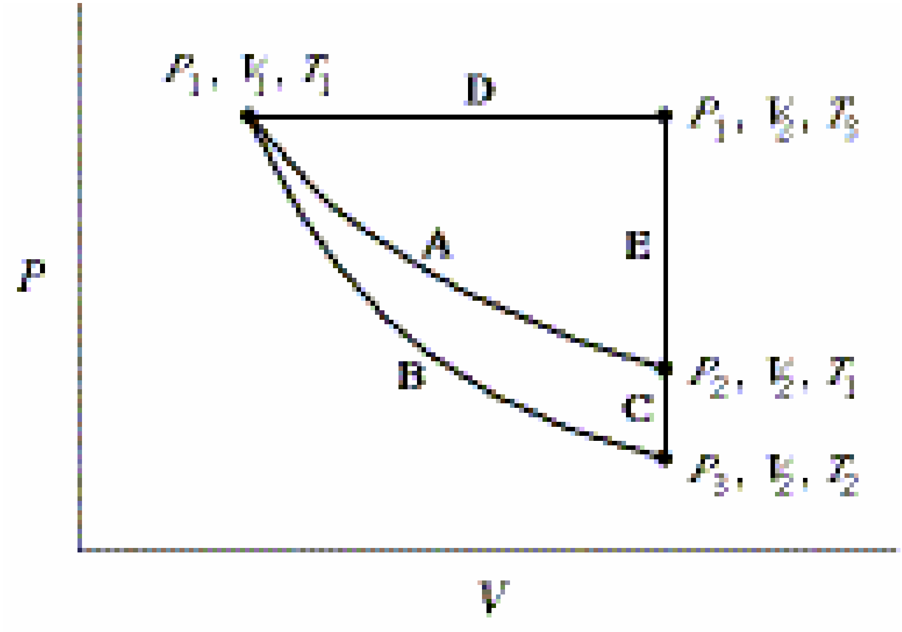
$$\frac{\delta q_{rev}}{T} = \frac{C_V(T)dT}{T} + \frac{nR}{V}dV$$

Let q/T be the new state function; <u>entropy</u>…

An old friend shows us S is a state function…

Path A vs. Path B+C vs. Path D+E

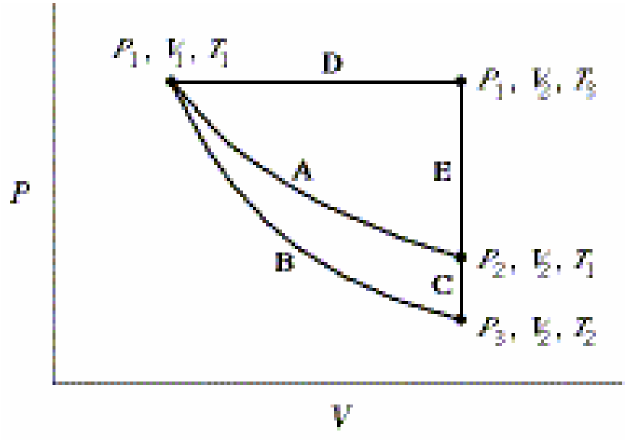
Is the change in entropy for these different paths?



Path A

Recall (from FL-10):

Path B + C



Path B

Adiabatic Expansion

$$\boxed{\Delta S_B = 0}$$

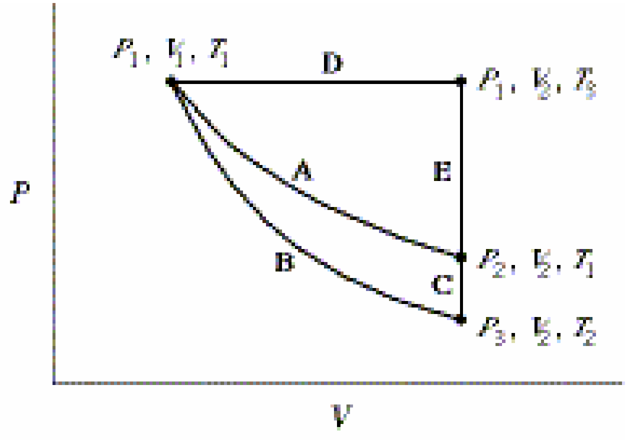
Path C

Recall (from FL-12) $q_{rev,C} = \Delta U_C = \int_{T_2}^{T_1} C_V(T)dT$

So… $$\Delta S_C = \int_1^2 \frac{\delta q_{C,rev}}{T} = -\int_{T_1}^{T_2} \frac{C_V(T)}{T}dT$$

Recall (from FL-16) $\int_{T_1}^{T_2} \frac{C_V}{T}dT = -nR\int_{V_1}^{V_2} \frac{1}{V}dV$

Path D + E



Path D+E

$$\delta q_{rev,D+E} = \delta q_{rev,D} + \delta q_{rev,E} = P_1 dV$$

$$\Delta S = \int_1^2 \frac{\delta q_{rev,D+E}}{T}$$

So…

$$\Delta S_{D+E} = P_1 \int_{V_1}^{V_2} \frac{dV}{T} \xrightarrow{\frac{1}{T} = \frac{nR}{P_1 V}} \Delta S_{D+E} = nR \int_{V_1}^{V_2} \frac{dV}{V}$$

Entropy and disorder

$$\Delta S = \int_1^2 \frac{\delta q_{rev}}{T}$$

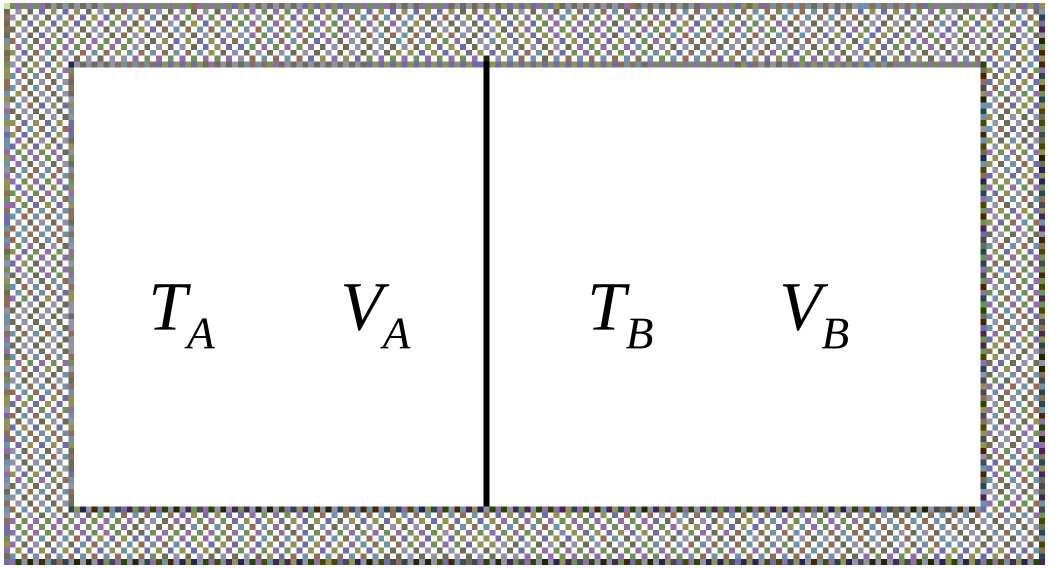
Entropy is related to the disorder of the system. If you add energy, as heat to a system, then its entropy increases because the thermal disorder increases.

Energy delivered at lower T contributes more to an entropy increase than energy delivered at higher T.

Entropy and Spontaneity … One Case

Energy as heat will flow spontaneously from a region of high temperature to a region of low temperature. **What is the role of entropy?**

Consider an isolated two compartment system



Both compartments are in equilibrium but not with each other

In an isolated system:

The system can do no work and can have no work done to it.

There is no exchange of energy with the surroundings.

(i.e., we can learn about spontaneity due to S alone… and not worry about U or H

Evaluate the energy and entropy

$$dV_A = dV_B = 0$$

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

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

$$dU_A = -dU_B$$

Why?

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

$T_B > T_A$, dU_B ?, dS ?

$T_B < T_A$, dU_B ?, dS ?

What does this tell us about spontaneity?

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

Entropy, unlike energy, is not conserved; it ***increases*** whenever a spontaneous process takes place. When the system reaches equilibrium **$dS = 0$**.

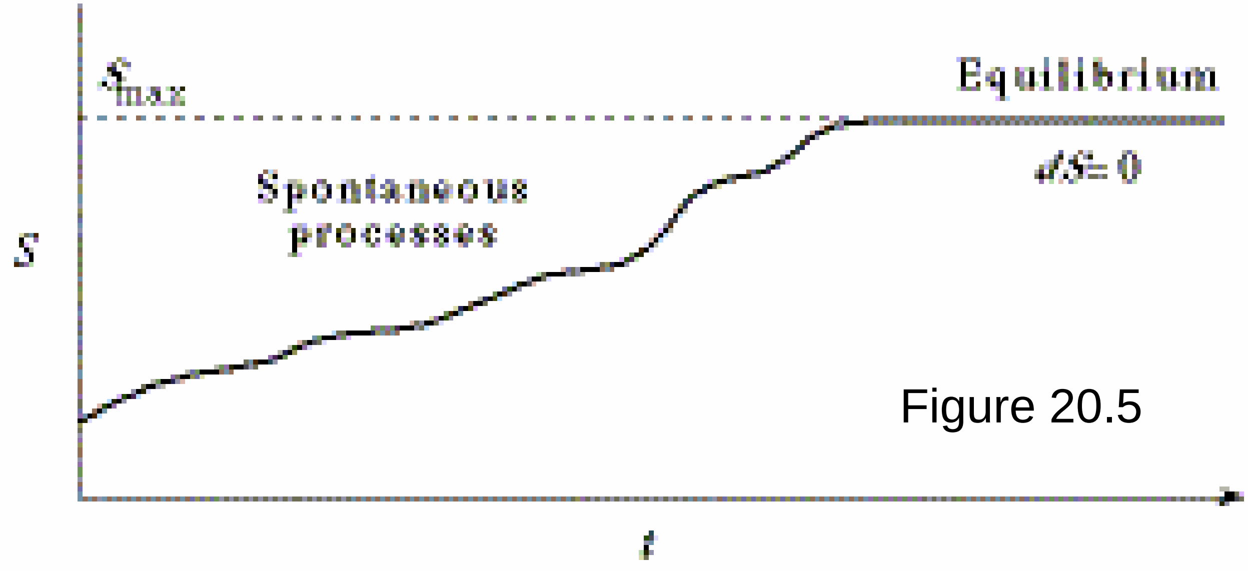


Figure 20.5

Isolated versus non-isolated…

Isolated system

$dS > 0$ For a spontaneous process

$dS = 0$ At equilibrium or for a reversible process

(Why?)

General system

There is exchange of heat with the surroundings.

dS becomes the sum of the system (prod) and the exchange:

$$dS = dS_{prod} + dS_{exchange}$$

The second law of thermodynamics…

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

$$dS \geq \frac{\delta q}{T}$$

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.

Other ways to write the 2^{nd} law mathematically:

$$dS > \frac{\delta q_{irr}}{T} \qquad dS = \frac{\delta q_{rev}}{T} \qquad \Delta S \geq \int \frac{\delta q}{T}$$

First and Second Law of Themodynamics

The First Law

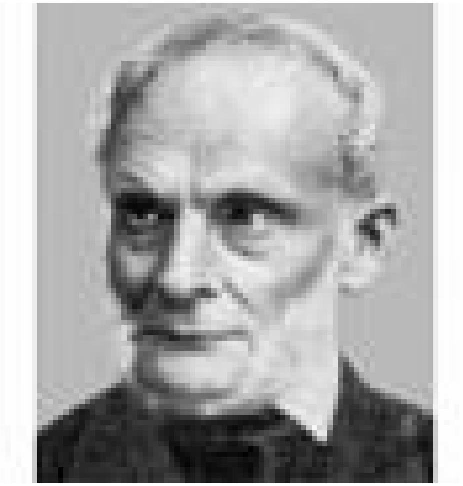
The energy of the universe is a constant…

$$\Delta U = q + w$$

The Second Law

The entropy is tending toward a maximum…

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



Rudolph Clausius

(see page 816!)