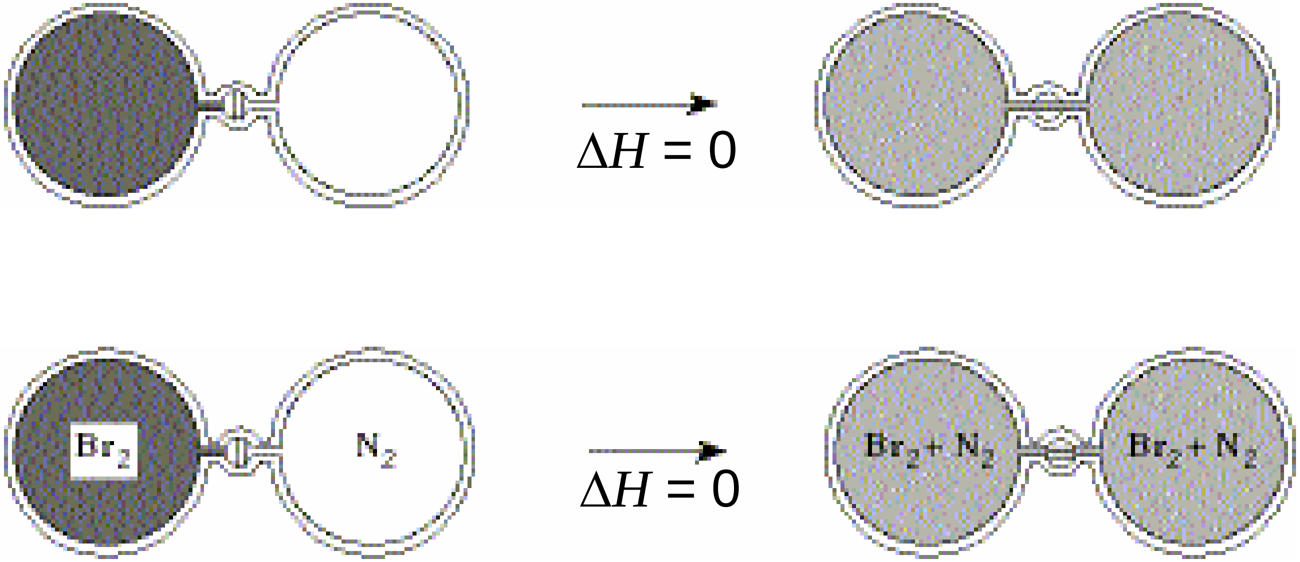
Spontaneous “Reactions”?

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…



$\Delta H = 0$

$\Delta H = 0$

$Ba(OH)_2$ (s) + 2 NH_4NO_3 (s) → $Ba(NO_3)_2$ (s) + 2 H_2O (l) + 2 NH_3 (aq) $\Delta H > 0$

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… **but q/T is!**

(Why?)

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

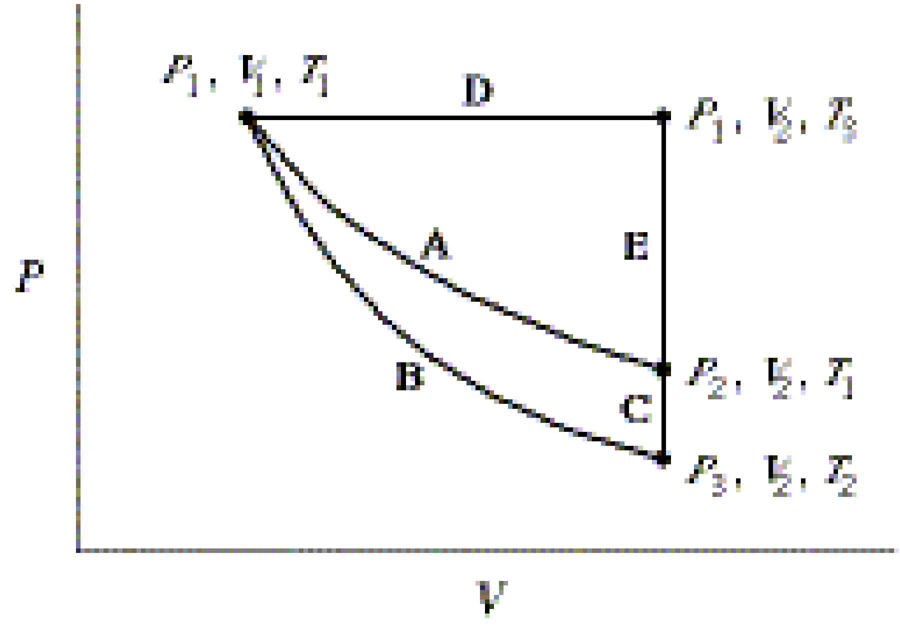
Let q/T be the new state function; <u>entropy</u>…

$$\boxed{dS \equiv \frac{\delta q_{rev}}{T}}$$

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 different for these different paths?



Path A

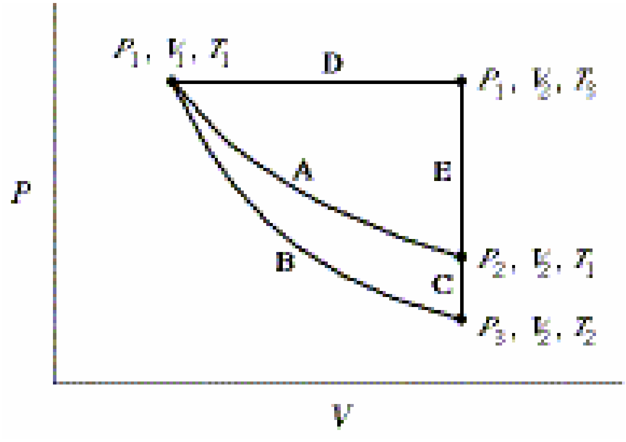
Recall (from FL-10):

$$\delta q_{rev,A} = \frac{nRT_1}{V} dV = nRT_1 \ln\frac{V_2}{V_1}$$

$$\Delta S_A = \int_1^2 \frac{\delta q_{A,rev}}{T_1} = \int_{V_1}^{V_2} \frac{1}{T_1}\frac{nRT_1}{V} dV$$

$$\boxed{\Delta S_A = nR\ln\frac{V_2}{V_1}}$$

Path B + C



Path B

Adiabatic Expansion

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

Path C

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

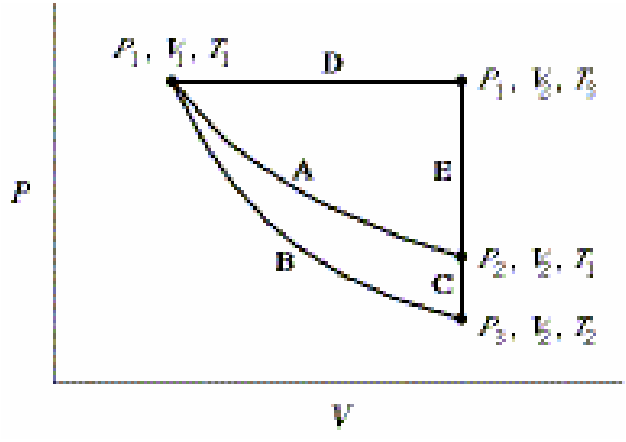
So…

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

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

$$\boxed{\Delta S_C = nR \ln \frac{V_2}{V_1}}$$

Path D + E



Path D+E

See FL-13

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

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

So…

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

$$\boxed{\Delta S_{D+E} = nR \ln \frac{V_2}{V_1}}$$

The entropy changes for all three **different** paths are exactly the same!

Entropy and disorder

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

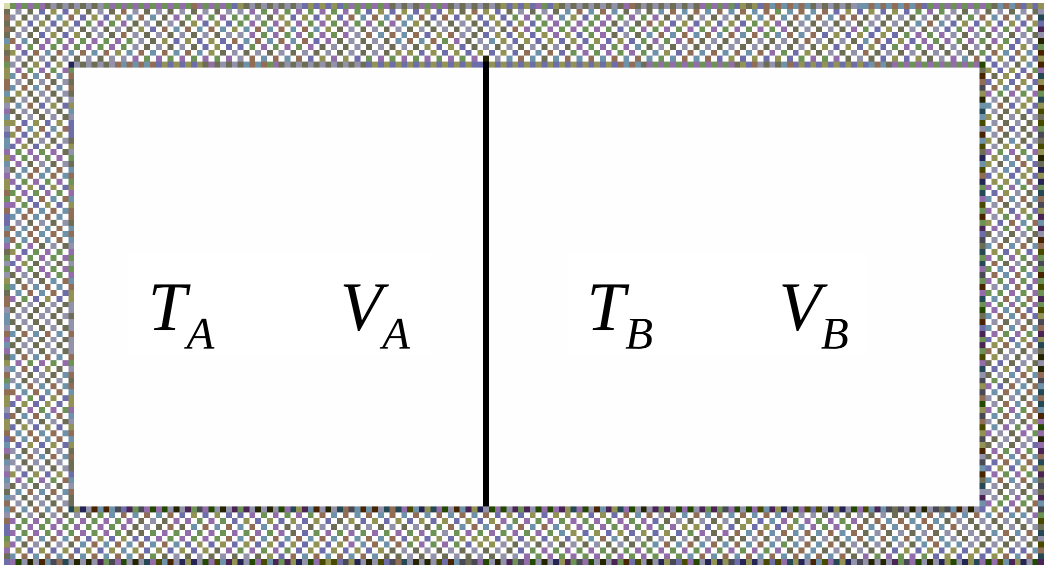
Entropy is related to the disorder of the system. If you add energy, as heat, to a system then its entropy increases because the thermal disorder increases.

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:

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

$$V_A = \text{constant}$$

$$V_B = \text{constant}$$

$$S = S_A + S_B$$

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 $dS = 0$.

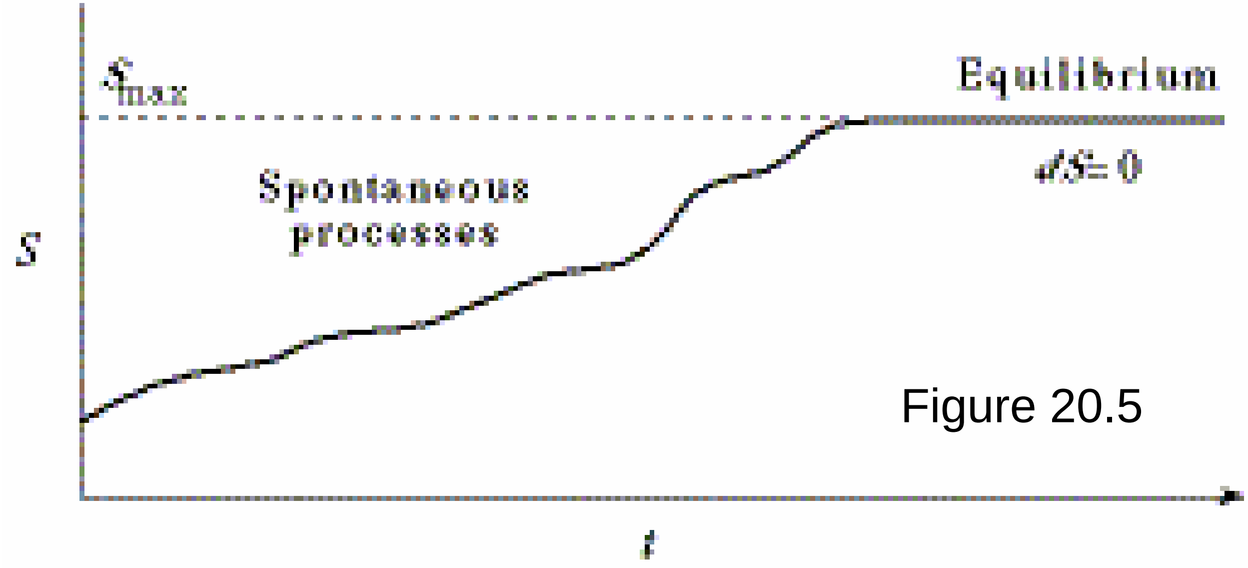


Figure 20.5

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:

$$dS = dS_{prod} + dS_{exchange} \quad \text{or} \quad dS = dS_{prod} + \frac{\delta q}{T}$$

Reversible Process:

$$\delta q = \delta q_{rev}, dS_{prod} = 0 \qquad dS = \frac{\delta q_{rev}}{T}$$

Irreversible/ Spontaneous Process:

$$dS_{prod} > 0, dS_{exch} = \frac{\delta q_{irr}}{T} \qquad dS > \frac{\delta q_{irr}}{T}$$

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 2nd 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!)

Entropy and Statistical Mechanics

The most famous equation of statistical thermodynamics:

$$S = k_B \ln W$$

Entropy is a state function related to disorder. Disorder can be expressed in a number of ways. We'll discuss one (statistical) way here…

Recall: The last time we had each hot chocolate (system) in the collection of hot chocolates (ensemble) with the same N, V, and T (*canonical ensemble*).

Now: Let's consider an ensemble with the same N, V, and E (*microcanonical ensemble*).

Even though every system has the same energy, each system can be in different quantum states due to degeneracy.

$\Omega(E)$ is the degeneracy associated with energy E.

typically huge #

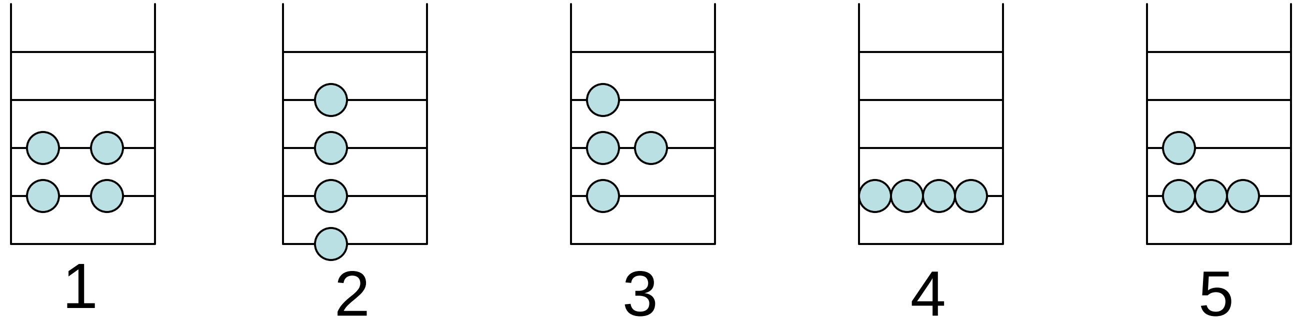
Application of statistics

Let W be the number of ways of having a_1 systems in state 1, a_2 in state 2, etc. (the systems are distinguishable).

$$W(a_1, a_2, a_3, \ldots) = \frac{A!}{a_1!a_2!a_3!\ldots} = \frac{A!}{\prod_j a_j!}$$

Imagine we have A = 4 (i.e., 4 systems) and 5 states…

○ = 1 system



$W_{min} =$

$W_{max} =$

$W =$ $W =$ $W =$ $W =$ $W =$

Entropy and *W*

$$S = k_B \ln W$$

For a perfectly ordered arrangement:

For a “completely” disordered arrangement:

Why ln *W*?

We know: $S_{total} = S_A + S_B$ & $W_{AB} = W_A W_B$

$$S_{total} = k_B \ln W_{AB} = k_B \ln W_A W_B = k_B \ln W_A + k_B \ln W_B = S_A + S_B$$

$$S = k_B \ln \Omega$$

This is the form using degeneracy.
(Derived in M&S: pg. 831)

Partition Functions and Entropy

$$S_{ensemble} = k_B \ln W = k_B \ln \frac{A!}{\prod_j a_j!}$$

$$= k_B A \ln A - k_B \sum_j a_j \ln a_j$$

From Math Chapter J (Eq 7 and 8)

$$\ln N! = \sum_{n=1}^{N} \ln n \qquad \ln N! = N \ln N - N$$

Stirling's approximation

Using: $S_{system} = \frac{S_{ensemble}}{A}$ and $p_j = \frac{a_j}{A}$

$$S_{ensemble} = k_B A \ln A - k_B \sum_j p_j A \ln p_j A$$

$$= k_B A \ln A - k_B \sum_j p_j A \ln p_j - k_B \sum_j p_j A \ln A$$

See pg 840-841

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

If all probabilities are 0 except one:

If all probabilities are equal :

S in terms of *Q*

$$p_j = \frac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)}$$

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

$$= -k_B \sum_j \frac{e^{-\beta E_j}}{Q}\left(-\beta E_j - \ln Q\right)$$

$$= \beta k_B \sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k_B \ln Q}{Q} \sum_j e^{-\beta E_j}$$

Now we have *S* in terms of *Q*…

$$\boxed{S = \frac{U}{T} + k_B \ln Q}$$

S for an ideal gas…

$$Q(N,V,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \frac{V^N}{N!} g_{e1}$$

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q$$

$$\Downarrow$$

$$\bar{S} = \frac{5}{2} R + R \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{\bar{V}}{N_A} g_{e1}\right]$$

Section 20-9

As promised on BZ-6

- Proof of:

$$\beta = \frac{1}{k_B T}$$

- And proof that:

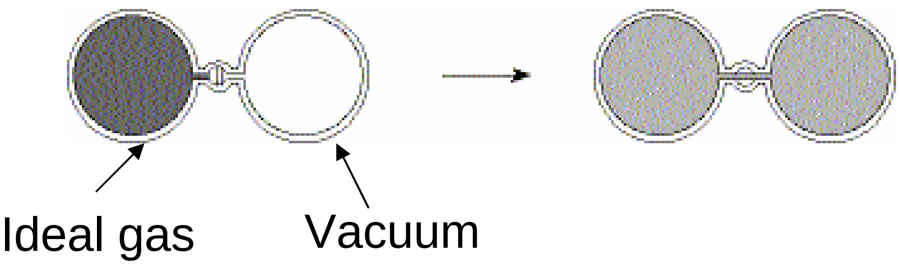
$$S = k_B \ln W \quad \text{and} \quad dS = \frac{\delta q_{rev}}{T}$$

are equivalent.

Entropy and Applications

The next few slides discuss some physical processes and the role of entropy in each process. (Chemical processes will be discussed in the next chapter.)

Start with: **An isothermal expansion of a gas into a vacuum…**



Since entropy is a <u>state function</u>, we can use the following equation (even though the process isn't reversible!).

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

$$\delta q_{rev} = dU - \delta w_{rev}$$

$$dU = 0 \longleftarrow \text{(Why?)}$$

$$\delta w_{rev} = -\frac{nRT}{V} dV$$

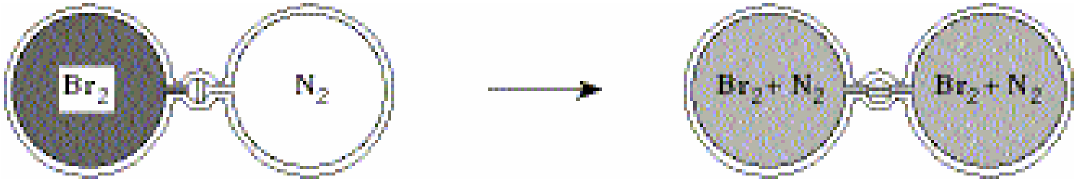
$$\Delta S = \int_1^2 \frac{\delta q_{rev}}{T} = -\int_1^2 \frac{\delta w_{rev}}{T}$$

$$= nR \ln \frac{V_2}{V_1}$$

$\boxed{\text{Is } \Delta S \text{ + or - ?}}$

Entropy of Mixing

Isothermal mixing of two ideal gases



$$\Delta S = \Delta S_{N_2} + \Delta S_{Br_2}$$

$$\Delta S_{Br_2} = n_{N_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{Br_2}} = -n_{N_2} R \ln \frac{V_{Br_2}}{V_{N_2} + V_{Br_2}}$$

$$\Delta S_{N_2} = n_{N_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{N_2}} = -n_{N_2} R \ln \frac{V_{N_2}}{V_{N_2} + V_{Br_2}}$$

Mole fraction:

$$y_i = \frac{n_i}{n_{total}}$$

Since these are ideal gases, n is proportional to V and ΔS becomes:

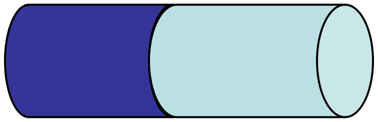
$$\Delta S = -n_{N_2} R \ln \frac{n_{N_2}}{n_{N_2} + n_{Br_2}} - n_{Br_2} R \ln \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}}$$

$$\boxed{\frac{\Delta_{mix} \overline{S}}{R} = -y_{N_2} \ln y_{N_2} - y_{Br_2} \ln y_{Br_2}}$$

+ or - ?

Heat Transfer

Heat transfer between two pieces of the same metal



Heat lost by hotter piece = heat gained by colder piece

$$U_h = U_c$$

$$C_V(T_h - T) = C_V(T - T_c)$$

Solve for T: $T = \dfrac{T_h + T_c}{2}$

What assumption made here?

$$\Delta S = \Delta S_h + \Delta S_c$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V\,dT}{T}$$

$$\boxed{\Delta S = C_V \ln \frac{(T_h + T_c)^2}{4T_h T_c}}$$

+ or - ?

Carnot Cycle and Heat Pumps/Engines

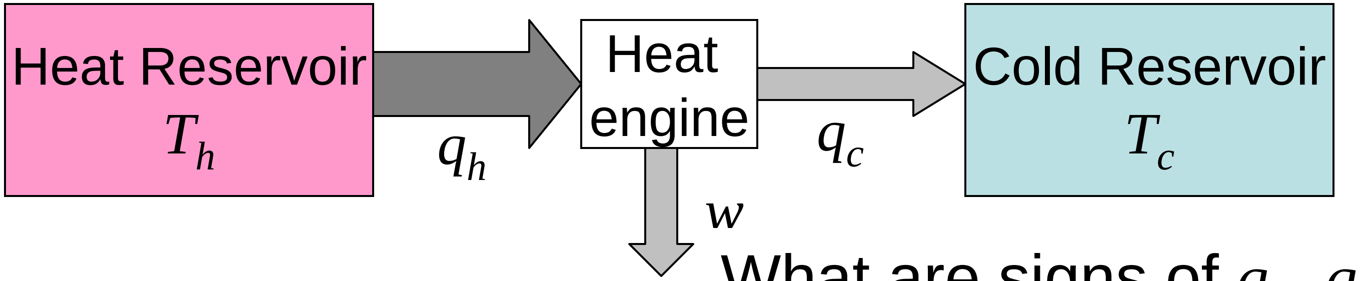
Sadi Carnot

Carnot used the following cycle to show that a heat engine can not convert all the heat energy supplied to it into mechanical work.

1. Isothermal expansion at T_h from V_1 to V_2
2. Adiabatic expansion from V_2 to V_3, T drops to T_c
3. Isothermal compression at T_c from V_3 to V_4
4. Adiabatic compression from V_4 to V_1, T rises to T_h

(You should be able to draw the Carnot cycle on a P-V diagram and solve for w, q, ΔU and ΔS for each step and the cycle as a whole).

What is a heat engine?



Heat Reservoir T_h

q_h

Heat engine

q_c

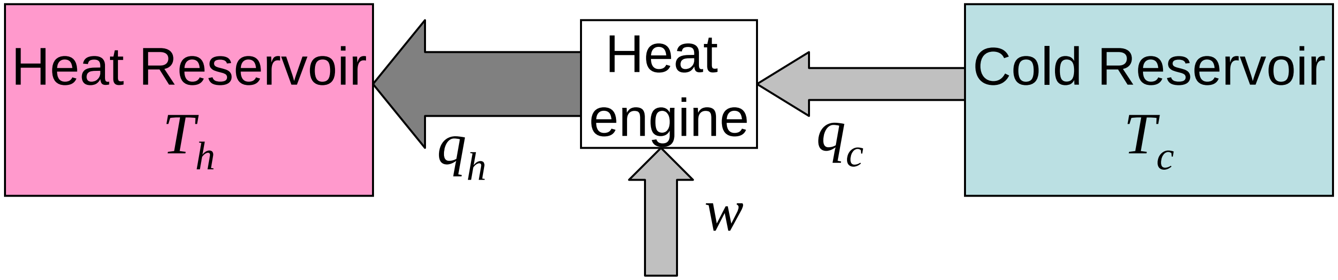
Cold Reservoir T_c

w

What are signs of q_h, q_c, and w?

Carnot Cycle and Heat Pumps/Engines 2

What is a heat pump?



What are signs of q_h, q_c, and *w*?

Consider the thermodynamics of the heat engine (or pump)…

$$\Delta U_{engine} = w + q_{rev,h} + q_{rev,c} = 0$$

$$\Delta S_{engine} = \frac{\delta q_{rev,h}}{T_h} + \frac{\delta q_{rev,c}}{T_c} = 0$$

Engine/Pump Efficiency

Sadi Carnot (and we) want to know how efficient this hypothetical heat engine (or pump) could be.

Maximum efficiency = work output / heat input

$$\eta = \frac{-w}{q_{rev,h}}$$

Using equations on bottom of SL-26

$$\eta = \frac{q_{rev,h} + q_{rev,c}}{q_{rev,h}} = 1 - \frac{T_c}{T_h}$$

$$\eta = \frac{T_h - T_c}{T_h}$$