Thurs: Seminar WS 264

Fri HW by 5pm

Second law of thermodynamics, entropy and temperature

The strong form of the second law of thermodynamics is:

> The equilibrium state of any isolated system will be the state for which the entropy is a maximum subject to any other constraints on the system.

Examples of constraints would be that the volume of the system is fixed or the total energy is fixed. We have already seen some implications of the second law.

Thermodynamic processes: Consider two systems initially isolated from each other and subsequently allowed to interact thermally

System A
System B → Water / Copper

immerse

water & copper
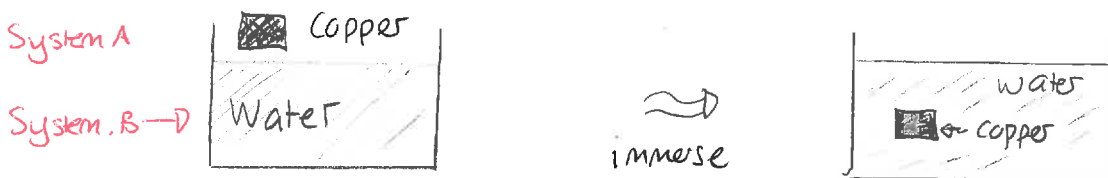
Combined system A + B is isolated. Has total entropy Si

Combined system A + B is isolated. Has total entropy SF

Then the total entropy will find a possibly new maximum after interaction. So the total entropy cannot decrease.

Thus:

For an isolated system, in any thermal process

$$\Delta S = Sf - Si \geq 0$$

Similarly for any quasistatic process

$$dS \geq 0$$

at all points along the process. These considerations constrain energy flows during any processes and inform us which way energy will flow.

Equilibrium between systems: Again when two systems interact we find that when they are in equilibrium with each other:

If energy can be exchanged $\left(\dfrac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} = \left(\dfrac{\partial S_B}{\partial E_B}\right)_{V_B, N_B}$

If volume can be exchanged $\left(\dfrac{\partial S_A}{\partial V_A}\right)_{E_A, N_A} = \left(\dfrac{\partial S_B}{\partial V_B}\right)_{E_B, N_B}$

Thermodynamic temperature   Whenever energy can be exchanged and two systems reach equilibrium we associate the same temperature with each system. We thus define the thermodynamic temperature of a system as:

$$T := 1 \Big/ \left(\dfrac{\partial S}{\partial E}\right)_{V,N}$$

The second law of thermodynamics guarantees that the two systems
- reach equilibrium at a common temperature
- energy flows from the higher temp to lower temp system

Units of entropy

We can see that

$$\left(\frac{\partial S}{\partial E}\right) = \frac{1}{T} \qquad \Rightarrow \qquad \frac{\text{entropy unit}}{J} = \frac{1}{K}$$

$$\Rightarrow \qquad \boxed{\text{entropy unit} = J/K}$$

Thermodynamic pressure

If two interacting systems can exchange volume then when they are in equilibrium their pressures must be the same. This suggests that pressure is related to $\left(\frac{\partial S}{\partial V}\right)_{E,N}$. Then observations suggest that the larger pressure system will gain volume over the lower pressure system. So we expect P to increase as $\left(\frac{\partial S}{\partial V}\right)_{E,N}$ increases. Then

units : pressure $\qquad N/m^2 = \frac{N \cdot m}{m^3} = \frac{J}{m^3}$

units : $\left(\frac{\partial S}{\partial V}\right)$ are $\frac{J/K}{m^3}$

If we include temperature as a factor then:

> The thermodynamic pressure for a system is
>
> $$P := T\left(\frac{\partial S}{\partial V}\right)_{E,N}$$
>
> provided $\qquad S = S(E,V,N)$

We will eventually see that the thermodynamic temperature and pressure have the same meaning (in specific cases) as the temperature and pressure that have been defined previously.

Measuring entropy changes

How could we measure entropy or at least changes in entropy?
Consider what the first law states:

$$dE = \delta Q - PdV$$

But

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV$$
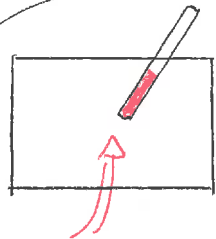
$$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV = \delta Q - PdV$$

Then

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = 1 \Big/ \left(\frac{\partial S}{\partial E}\right)_{V,N} = 1 \Big/ (1/T) = T. \quad \text{Thus}$$

$$T dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV = \delta Q - PdV$$

$$\Rightarrow dS = \frac{1}{T}\delta Q - \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_{S,N}\right] dV$$

This suggest that we consider a constant volume process: Then

$$dS = \frac{1}{T}\delta Q$$

Supply heat and observe
temperature and temperature
change.
- measure δQ
- T, dT

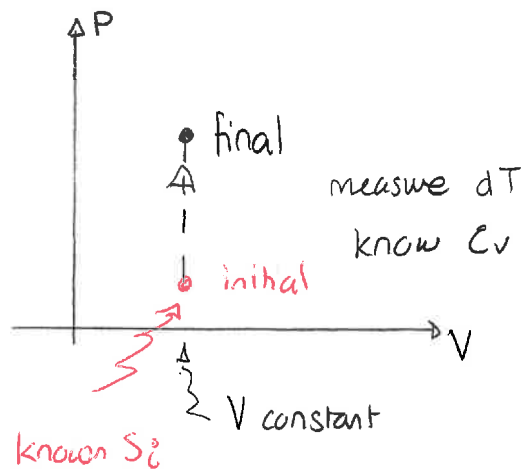$$\Rightarrow \quad \boxed{\Delta S = \int \frac{1}{T}\delta Q}$$

Then in a constant volume process

$$\delta Q = c_v dT$$

$$\Rightarrow \quad \boxed{\Delta S = \int \frac{c_v}{T} dT}$$

where c_v might depend on T.

This enables us to partly map S in the PV diagram

can get

$$S_f = S_i + \Delta S$$

along any vertical line.

We will consider how to map entropy changes "horizontally" later.

1 Entropy change for monoatomic ideal gas

A monoatomic ideal gas is heated at constant volume from temperature T_i to T_f. Determine an expression for the change in entropy of the gas.

Answer: Here

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v}{T}\, dT$$

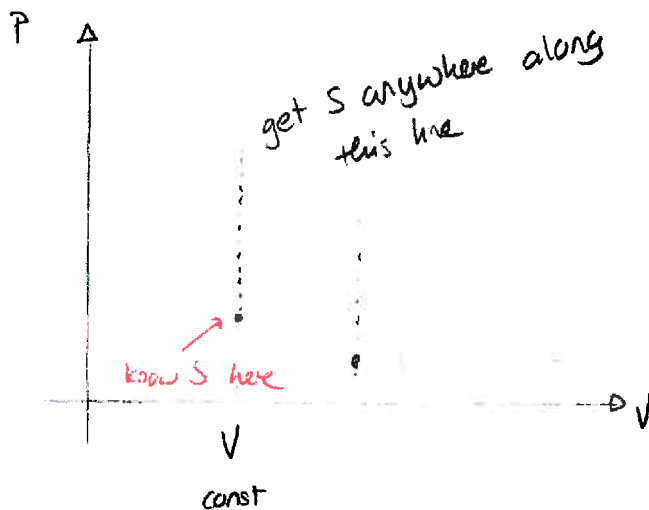and $\quad C_v = \frac{3}{2} N k \quad$ gives

$$\Delta S = \frac{3}{2} N k \int_{T_i}^{T_f} \frac{dT}{T}$$

$$= \frac{3}{2} N k \ln T \Big|_{T_i}^{T_f}$$

$$\Rightarrow \quad \Delta S = \frac{3}{2} N k \ln\left(\frac{T_f}{T_i}\right)$$

So now we can chart entropy as.

P

get S anywhere along
this line

know S here

V

V
const

Fundamental thermodynamic identity (part 1)

Suppose that the number of particles is fixed. Then $S = S(E,V)$ and

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

$$= \frac{1}{T} dE + \frac{P}{T} dV$$

$$\Rightarrow \quad TdS = dE + PdV$$

$$\Rightarrow \quad dE = TdS - PdV$$

This is true for all quasistatic processes in any gas and is called the <u>fundamental thermodynamic identity</u>

$$\boxed{dE = TdS - PdV}$$

We can use this to generate previous statements about temperature and entropy. For example

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

$$\Rightarrow \quad T = \left(\frac{\partial E}{\partial S}\right)_V \quad \Rightarrow \quad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$$

and $\quad -P = \left(\frac{\partial E}{\partial V}\right)_S \quad \Rightarrow \quad P = -\left(\frac{\partial E}{\partial V}\right)_S$

Entropy and heat flow

For any quasistatic infinitesimal process in a gas

$$dE = \delta Q - PdV$$

and

$$dE = TdS - PdV$$

implies.

For any quasistatic infinitesimal process:

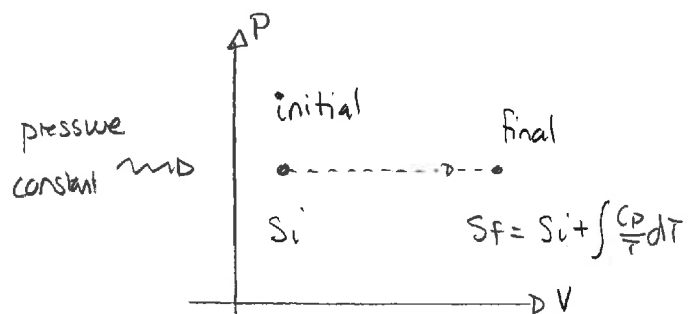$$\delta Q = TdS \qquad \text{and} \qquad dS = \frac{1}{T}\delta Q$$

Then for any process in general:

$$\Delta Q = \int TdS \qquad \text{and} \qquad \Delta S = \int \frac{1}{T}\delta Q$$

This means that for any process pressure is constant, $\delta Q = C_p dT$
and

$$\Delta S = \int \frac{C_p}{T} dT$$

process

This allows us to map entropy "horizontally"

pressure
constant ⟶

P

initial   final
• - - - - - - - - • - - •

S_i $S_f = S_i + \int \frac{C_p}{T} dT$

⟶ V

2 System plus bath: entropy changes

A heat bath/reservoir is a system, usually an environment, whose temperature stays fixed while it exchanges heat with another typically much smaller system. Consider a 2.00 kg block of aluminum which is initially at a temperature of 100° C. This is placed in contact with air (the bath) whose temperature is 20.0° C. The specific heat capacity of aluminum is 897 J/K· kg. The aluminum comes to equilibrium with the air.

a) Determine the heat lost by the aluminum.

b) Determine the change in entropy of the aluminum, assuming that the heat capacity is constant over this range.

c) Determine the change in entropy of the aluminum plus the air. Does this satisfy the second law of thermodynamics?

Answer: a) $\qquad \delta Q = c \, dT \qquad$ and $\quad c$ is constant

$$\Rightarrow Q = \int c \, dT = c \int dT = c \, \Delta T$$

Now $\quad c = 897 \text{ J}/\text{K·kg} \times 2.00 \text{kg} = 1.79 \times 10^3 \text{ J}/\text{K}.$

Then: $\quad Q = 1.79 \times 10^3 \text{ J}/\text{K} \, (-80 \text{k}) = -1.43 \times 10^5 \text{ J}.$

b) $\quad \Delta S_{Al} = \int_{T_i}^{T_F} \frac{c}{T} \, dT = c \int_{T_i}^{T_F} \frac{dT}{T} = c \ln\left(\frac{T_F}{T_i}\right)$

$$\Rightarrow \Delta S_{Al} = 1.79 \times 10^3 \text{ J}/\text{K} \, \ln\left(\frac{273+20}{273+100}\right) = -432 \text{ J}/\text{K}$$

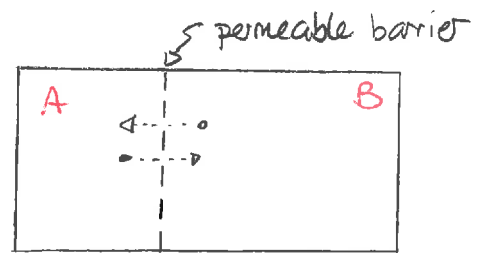c) $\quad \Delta S_{Bath} = \int \frac{1}{T} \delta Q = \frac{1}{T} \int \delta Q = \frac{Q}{T}$

Then $\Delta S_{Bath} = \dfrac{1.43 \times 10^5 \text{ J}}{293 \text{K}} = 488 \text{ J}/\text{K}.$

The total entropy change is $\quad \Delta S = \Delta S_{Al} + \Delta S_{Bath}$

$$= -432 \text{ J}/\text{K} + 488 \text{ J}/\text{K}$$

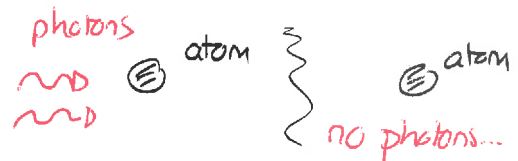$$= 56 \text{ J}/\text{K} \geq 0 \quad \underline{\text{YES}}$$

Systems with variable particle number

In some cases particles can be exchanged between systems. This includes

1) systems connected by permeable barriers

permeable barrier

A   B

2) systems in which chemical reactions can occur

3) systems consisting of photons interacting with matter

photons   atom   atom

no photons...

In general the energy of a system increases when the number of particles increases. The first law will require some modification to manage this. Consider a gas at a fixed volume and suppose that it is isolated. Then if molecules are added

$$\Delta E = Q + W$$

$$\Rightarrow \Delta E = 0 + 0 \Rightarrow \Delta E = 0$$

But $\Delta E \neq 0$ since it increases with N. We need to modify the first law to account for this. This will be done via entropy.

We again consider two systems that can interact and exchange particles. Then:

$$S = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B)$$

and $E = E_A + E_B =$ constant

$V = V_A + V_B =$ constant

$N = N_A + N_B =$ const.

By the usual derivation

$$\left(\frac{\partial S_A}{\partial N_A}\right)_{E_A, N_A} = \left(\frac{\partial S_B}{\partial N_B}\right)_{E_B, V_B}$$

when the system is in equilibrium. We then define a physical quantity that captures this:

> The chemical potential of a system is:
> $$\mu = -T \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

units: J

Then we have

> Two systems are in equilibrium $\Rightarrow$ the chemical potentials of the systems are equal

We can now consider which way systems exchange particles. Consider two systems at the same temperature and whose volumes are fixed. Then

$$dS = dS_A + dS_B$$

$$= \left(\frac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} dE_A + \left(\frac{\partial S_A}{\partial V_A}\right)_{E_A, N_A} dV_A + \left(\frac{\partial S_A}{\partial N_A}\right)_{E_A, V_A} dN_A$$

$$+ \text{ similar for } B$$

$$= \frac{1}{T_A} dE_A + \frac{P_A}{T_A} dV_A - \frac{\mu_A}{T_A} dN_A$$

$$+ \frac{1}{T_B} dE_B + \frac{P_B}{T_B} dV_B - \frac{\mu_B}{T_B} dN_B.$$

Now $dE = 0 \Rightarrow dE_A + dE_B = 0 \Rightarrow dE_B = -dE_A$

Then:

$$dS = \left[\frac{1}{T_A} - \frac{1}{T_B}\right] dE_A + \left[\frac{P_A}{T_A} - \frac{P_B}{T_B}\right] dV_A - \left[\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right] dN_A$$

And if $T_A = T_B = T > 0$ and V_A is constant:

$$dS = -\frac{1}{T}\left[\mu_A - \mu_B\right] dN_A$$

So $dS \geqslant 0$

$$\Rightarrow -\frac{1}{T}\left[\mu_A - \mu_B\right] dN_A \geqslant 0$$

$$\Rightarrow \left[\mu_A - \mu_B\right] dN_A \leq 0$$

So if $\mu_B > \mu_A$ then $dN_A > 0$. We see that

Particles flow from a system with higher chemical potential to one with lower chemical potential

Fundamental thermodynamic identity

Again:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

$$= \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\Rightarrow \boxed{dE = T dS - P dV + \mu dN}$$

This is the fundamental thermodynamic identity. Note that

$$dE = \delta Q - P dV + \mu dN$$