

I last time

II Equilibrium from the statistical perspective

III Equilibrium between phases

Meeting

• Found

$f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v}$ = mean # of molecules w/ com positions between \vec{r} and $\vec{r} + d\vec{r}$ and velocity between \vec{v} and $\vec{v} + d\vec{v}$.

$$f(\vec{v}) d^3\vec{v} d^3\vec{r} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m\vec{v}^2}{2kT}} d^3\vec{r} d^3\vec{v}$$

• Similarly

$$g(v_x) dv_x = n \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{mv_x^2}{2kT}} dv_x$$

• Finally $F(v) dv$ = mean # of molecules per unit volume with a speed between v and $v + dv$.

$$F(v) dv = 4\pi f(v) v^2 dv \\ = 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv$$

• You should check that:

$$\bar{v} = \sqrt{\frac{3kT}{\pi m}}$$

$$v_{rms} = \sqrt{v^2} = \sqrt{\frac{3kT}{m}}$$

$$v_{max} = \sqrt{\frac{2kT}{m}}$$

I caused some confusion last Wednesday — not sure quite how now — but the distinctions were

as follows: We have done each of the following

$$Z' = \int \dots \int e^{-\beta E} \frac{d^3x \dots d^3p}{h^{3N}}$$

the whole gas

$P(\vec{r}, \vec{p}) \delta^3 \vec{r} \delta^3 \vec{p} = \text{prob. for 1 molec. in range of } \vec{r} \text{ to } \vec{r} + d\vec{r}, \vec{p} \text{ to } \vec{p} + d\vec{p}$

$$f(\vec{r}, \vec{v}) = N P(\vec{r}, \vec{p}(\vec{v}))$$

mean # of molecules in range.

In other words, when you perturb the system you find

$$\Delta S = S - S_{\text{max}} \leq 0$$

Let's ask "why?" again.

1st version: "Isolated system"

describe state by y

$\Omega(y) = \# \text{ of states } \in [y, y + \delta y]$

$$S(y) = k \ln \Omega(y)$$

II We're going to run 3 very parallel arguments in a row.

Pay attention so that you can do the last one yourselves.

What is equilibrium? Plethora of answers. Fig. 1

$$\Delta S \geq 0$$

So equilib = maximum entropy configuration

iii) Basic postulate:

$$P(y) \propto \Omega(y) = e^{S/k}$$

IF y can freely adjust it will and evolves to y ; location of S_{max} .

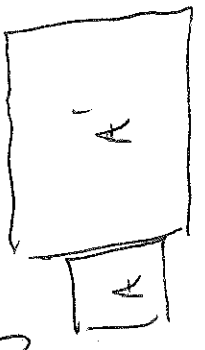
(iii) Notice that

$$\frac{P(y)}{P_{\text{max}}} = e^{-\Delta S/k}$$

Captures 2nd law quantitatively. — Can even look at fluctuations of y .

2nd version: Contact with heat bath

Thermodynamic version:



$$\Delta S^{(co)} \geq 0$$

$$\Delta S^{(co)} = \Delta S + \Delta S'$$

$$\Delta S' = \frac{(-Q)}{T_0}$$

For $T_0 > 0$, we have

$$\Delta S^{(co)} \geq 0$$

and so

$$-\Delta F_0 \geq W$$

The most work the system can do is bound by the free energy — this is the reason for the name!

Let's further specialize to $W=0$ then

$$\Delta F_0 \leq 0 \quad \left(\begin{array}{l} \text{free energy} \\ \text{spontaneously} \\ \text{decreases} \end{array} \right)$$

$$Q = \Delta E + W$$

So,

$$\Delta S^{(co)} = \Delta S + \frac{-\Delta E - W}{T_0}$$

$$= \frac{\Delta S T_0 - \Delta E - W}{T_0}$$

$$= \frac{\Delta (S T_0 - \bar{E}) - W}{T_0}$$

$$= -\frac{\Delta F_0 - W}{T_0}$$

and so equilibrium is when the free energy is

$$F_0 = \text{minimum}$$

describe state by y

$$\Delta S = S(y) - S(y_1) \quad \text{when } W=0$$

$$\Delta E = E(y) - E(y_1) = Q$$

$$\Delta S^{(co)} = -\frac{\Delta F_0}{T_0}$$

(iii)

$$P(y) \propto \Omega(y) = e^{S(y)/k}$$

(iii) But from setup

$$S^{(0)}(y) = S^{(0)}(y_1) - \frac{F_0(y) - F_0(y_1)}{T_0}$$

and $P(y) \propto e^{-F_0(y)/kT_0}$

We recover the claim that equilibrium

(max prob. config.) is when

$$F_0 = \text{minimum}$$

W^* = work done not due to vol. change.

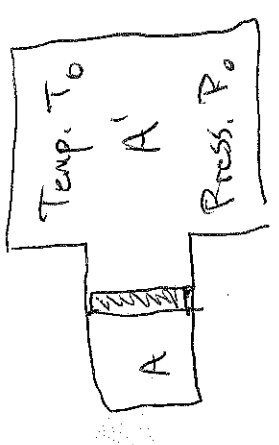
$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0}$$

$$= \frac{\Delta S T_0 - \Delta E - P_0 \Delta V - W^*}{T_0}$$

$$= \frac{1}{T_0} [\Delta(S T_0 - E - pV) - W^*]$$

$$= \frac{-\Delta G_0 - W^*}{T_0}$$

3rd Version: Heat bath and $P^4/6$ pressure reservoir.



Thermodynamic Version

$$\Delta S^{(0)} = \Delta S + \Delta S' \geq 0$$

$$Q = \Delta E + P_0 \Delta V + W^*$$

and so we see

$$-\Delta G_0 \leq W^*$$

Another free energy - the free energy to do work other than vol. expansion in constant P_0 environment.

If $W^* = 0$,

$$\Delta G_0 \leq 0$$

So, in this setting, equilibrium is

$$G_0 = \text{minimum}$$

describe state by y } setup

$$\Delta S = S(y) - S(y_1)$$

$$\Delta S^{(co)} = - \frac{\Delta G_0}{T_0}$$

(ii)

$$P(y) \propto \Omega(y) = e^{S^{(co)}(y)/k}$$

$$S^{(co)}(y) = S^{(co)}(y_1) - \frac{G_0(y) - G_0(y_1)}{T_0}$$

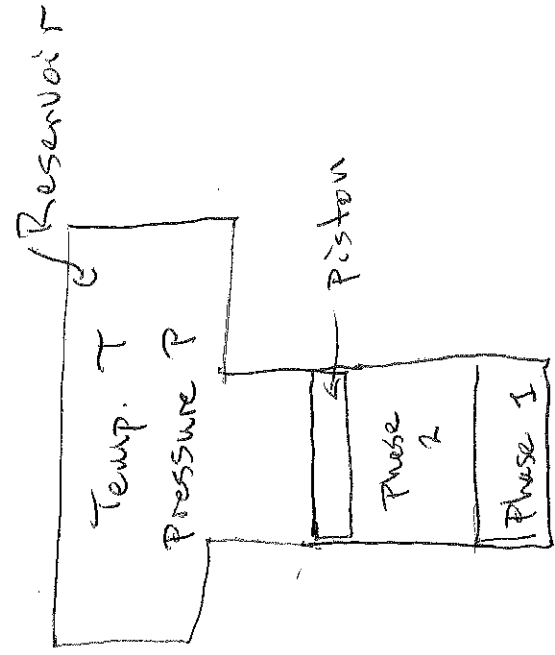
and

$$P(y) \propto e^{-G_0(y)/kT}$$

and again

$$G_0 = \text{minimum}$$

at equilibrium!



and so,

$$dG = g_1 dv_1 + g_2 dv_2 = 0$$

$$\Rightarrow (g_1 - g_2) dv_1 = 0 \Rightarrow g_1 = g_2$$

III For a constant T and P environment equilibrium is obtained when

$$G = E - TS + pV = \text{minimum}$$

Let ν_i = number of i type moles

$$g_i(T, p) = \text{Gibbs free E per mole of phase } i \text{ at } T \text{ and } p$$

Certainly $\nu_1 + \nu_2 = V = \text{constant}$

Hence the condition for equilib. between two phases is simply

$$g_1 = g_2$$

Useful to look at this on a P vs T diagram. If $g_1 < g_2$ it all goes to phase 1 and

$$G = n g_1$$

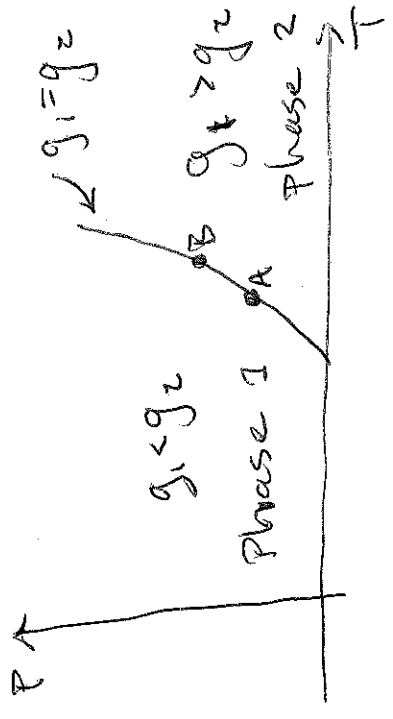
"phase equilibrium line" as follows

$$g_1(T, P) = g_2(T, P) \text{ at A}$$

$$g_1(T + \Delta T, P + \Delta P) = g_2(T + \Delta T, P + \Delta P) \text{ at B}$$

or $dg_1 = dg_2$

This will be the starting



If $g_1 = g_2$ any amount of phase 1 can coexist with any amount of phase 2

We can find the $g_1 = g_2$

point for our derivation of the Clausius - Clapeyron equation next time.