

## Lecture 5

Last time, discussed thermodynamic potentials

Idea that functional form of free energy

= energy available to do work

depends on system constraints

And that equilibrium occurs when system has

no free energy available

⇒ thermo potential is minimum

Look at a couple examples:

### Entropy of mixing

Recall  $S \equiv \int_{\text{rev}} \frac{\delta Q}{T} + \text{const}$  : purely thermal

Can make connection to disorder

First: what is  $S$  for ideal gas?

Know  $E = \alpha NkT$  and  $PV = NkT$

Can get  $S$  from  $C_V = \left(\frac{\partial E}{\partial T}\right)_V = \alpha Nk$

also derived  $C_V = T \left(\frac{\partial S}{\partial T}\right)_V$

so  $\left(\frac{\partial S}{\partial T}\right)_V = \alpha \frac{Nk}{T}$

But  $S$  depends on  $V$  too:

Maxwell relations say  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V}$

$$So \quad dS = \alpha \frac{Nk}{T} dT + \frac{Nk}{V} dV$$

\* if you're going to integrate a differential, make sure you have all the terms!

$$S = \int \left( \frac{\partial S}{\partial T} \right)_V dT + K_1(V)$$

$$= \alpha Nk \ln T + K_1(V)$$

$$or \quad S = \int \left( \frac{\partial S}{\partial V} \right)_T dV + K_2(T)$$

$$= Nk \ln V + K_2(T)$$

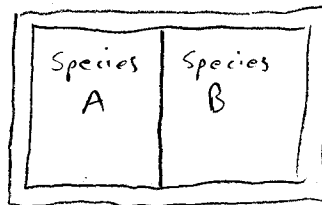
(compare, see  $S = \alpha Nk \ln T + Nk \ln V + const$ )

$$or \quad \boxed{S = Nk \ln \left( \frac{T}{T_0} \right)^{\alpha} \left( \frac{V}{V_0} \right) + S_0}$$

where  $S_0, T_0, V_0 =$  reference values

Now think about how entropy changes when gases mix:

Insulated box  
w/ two compartments:



Two ideal gases

Initially at same  $P_i, T_i$

Remove barrier, allow to equilibrate (irreversibly)

Get same  $T = T_f$

$$P = P_A + P_B = P_f$$

But entropy changes

Let's use Gibbs free energy to calculate  
since  $P, T, \& N$  are constant

$$dG = -SdT - XdY + \mu dN$$

$$\text{So } S = - \left( \frac{\partial G}{\partial T} \right)_{Y \rightarrow P}$$

Calculate  $G$  from  $G = E - TS - PV$

$$= \alpha NkT - T \left[ S_0 + Nk \ln \left( \frac{T}{T_0} \right)^{\alpha} \left( \frac{V}{V_0} \right) \right] - NkT$$

Express as fun of  $P$   
to make  $\left( \frac{\partial G}{\partial T} \right)_P$  easy

$$\frac{V}{V_0} = \left( \frac{NkT}{P} \right) \left( \frac{P_0}{NkT_0} \right) = \frac{P_0}{P} \frac{T}{T_0}$$

$$\begin{aligned} \text{So } G &= (\alpha - 1)NkT - TS_0 - NkT \ln \left( \frac{T}{T_0} \right)^{\alpha+1} + NkT \ln \frac{P}{P_0} \\ &= f(T) + NkT \ln \frac{P}{P_0} \end{aligned}$$

So in our mixing system, initially

$$G_A = f_A(T) + N_A kT \ln \frac{P}{P_0}$$

$$G_B = f_B(T) + N_B kT \ln \frac{P}{P_0}$$

After barrier removed,  $P_A \rightarrow \frac{N_A}{N} P$

$$P_B \rightarrow \frac{N_B}{N} P$$

$$N = N_A + N_B$$

$$\text{So } G \rightarrow f_A(T) + f_B(T) + N_A kT \ln \frac{N_A}{N} \frac{P}{P_0} + N_B kT \ln \frac{N_B}{N} \frac{P}{P_0}$$

and

$$\Delta G = G(\text{final}) - G(\text{init}) = N_A kT \left[ \ln \frac{N_A}{N} \frac{P}{P_0} - \ln \frac{P}{P_0} \right] \\ + N_B kT \left[ \ln \frac{N_B}{N} \frac{P}{P_0} - \ln \frac{P}{P_0} \right]$$

$$\Delta G = N_A kT \ln \frac{N_A}{N} + N_B kT \ln \frac{N_B}{N}$$

Finally,

$$\Delta S = - \left( \frac{\partial(\Delta G)}{\partial T} \right)_P = -N_A k \ln \frac{N_A}{N} - N_B k \ln \frac{N_B}{N}$$

See  $\Delta S > 0$

$\Rightarrow$  removing order increases entropy,  
even w/ no heat or work involved

(Note, you could have gotten this as easily by  
calculating  $\Delta S$  directly from formula  
Either way is fine.)

But wait a second,

What if A & B are the same substance?

Still get  $\Delta S > 0$ , but no physical change  
to system

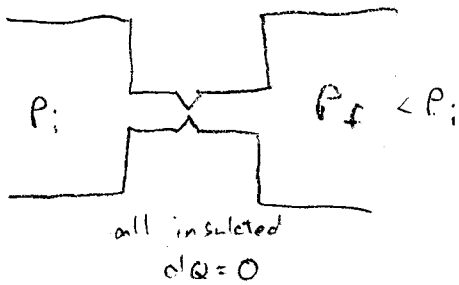
For this case, result is wrong: Gibbs paradox

Resolved in stat mech, from QM of indistinguishable  
particles

(answer: So depends on N)

Consider a more practical application:  
Joule-Thompson effect

Squirt non-ideal gas through thin nozzle



Gas expands irreversibly  
into final chamber

For ideal gas, free expansion has no effect on  $T$

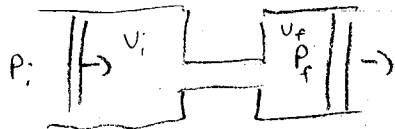
But real gases have molecular attraction, repulsion  
Repulsive force does work on gas in expansion  
 $\Rightarrow dE > 0$ , heating

Gas does work on attractive force  
 $\Rightarrow dE < 0$ , cooling

Dominant effect depends on interaction  
parameters &  $T + P$  of gas

How to analyze?

Imagine pistons moving gas through nozzle:



$$W = \int_0^{V_f} P_f dV_f + \int_{V_i}^0 P_i dV_i = P_f V_f - P_i V_i$$

= work done by system

Internal forces don't contribute to this

Have  $dQ=0$ , so  $\Delta E = -W$

$$E_f - E_i = P_f U_f - P_i V_i$$

$$E_f - P_f V_f = E_i - P_i V_i$$

$$H_f = H_i$$

Enthalpy is constant in this process

Makes sense:  $P, S, N$  constant  
 $\hookrightarrow$  well, sort of

So enthalpy is right potential

Neither storing nor retrieving work, so  $H = \text{const}$

Actual process is irreversible

To analyze, consider hypothetical reversible path

$$\text{Then } dH = T dS + V dP = 0$$

Really interested in  $(P, T)$

$$\text{write } dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dH = T \left(\frac{\partial S}{\partial T}\right)_P dT + \left[T \left(\frac{\partial S}{\partial P}\right)_T + V\right] dP = 0$$

Recognize  $C_p = T \left(\frac{\partial S}{\partial T}\right)_P$

$$\text{Also Maxwell gives } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha_P$$

$$\text{So } C_p dT + [-V T \alpha_p + V] dP = 0$$

and 
$$\left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (T \alpha_p - 1) \equiv \mu_J$$

"Joule-Thompson coefficient,"

Says how T changes with P

Note for ideal gas, 
$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \frac{\partial}{\partial T} \left( \frac{NkT}{P} \right)$$

$$= \frac{Nk}{PV} = \frac{1}{T}$$

So  $\mu_J = 0$  as expected

Consider instead van der Waals gas

$$NkT = \left( P + a \frac{N^2}{V^2} \right) (V - Nb)$$

$a$  &  $b$  describe interactions

In hw, work out  $\alpha_p$  here exactly.

I'll do in approximation of small  $a, b$ :

Need 
$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{\left( \frac{\partial P}{\partial V} \right)_T}$$

$$NkT = PV + a \frac{N^2}{V} - bNP - ab \frac{N^3}{V^2} \quad \text{drop}$$

$$\left( \frac{\partial P}{\partial V} \right)_T = \frac{1}{Nk} \left[ P - a \frac{N^2}{V^2} \right]$$

$$= \frac{1}{Nk} \left[ P - \frac{a}{v^2} \right]$$

$v \equiv \frac{V}{N}$  volume/particle

Use 
$$P = \frac{NkT}{V - Nb} - a \frac{N^2}{V^2} = \frac{kT}{v - b} - \frac{a}{v^2}$$

Taylor expand  $\frac{1}{v-b} \rightarrow \frac{1}{v} \left(1 + \frac{b}{v}\right)$

$$\text{so } p = \frac{kT}{v} + kT \frac{b}{v^2} - \frac{a}{v^2}$$

$$\text{and } \left(\frac{\partial T}{\partial v}\right)_p = \frac{1}{Nk} \left[ \frac{kT}{v} + kT \frac{b}{v^2} - \frac{2a}{v^2} \right]$$

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p = \frac{Nk}{v} \frac{1}{\frac{kT}{v} + kT \frac{b}{v^2} - \frac{2a}{v^2}}$$

$$= \frac{1}{T} \frac{1}{1 + \frac{b}{v} - \frac{2a}{kTv}}$$

$$\approx \frac{1}{T} \left[ 1 - \frac{b}{v} + \frac{2a}{kTv} \right]$$

$$\text{So } \mu_J = \frac{v}{c_p} (T\alpha_p - 1)$$

$$= \frac{v}{c_p} \left( -\frac{b}{v} + \frac{2a}{kTv} \right)$$

$$\boxed{\mu_J = \frac{N}{c_p} \left( \frac{2a}{kT} - b \right)} \quad (\text{weak interactions})$$

See that  $a$  leads to heating,  $b$  to cooling

Always get cooling at low  $T$ , heating at high  $T$

Put in some numbers next time

## Comments about HW

1) How long did assignment take?

2) One important point was to see how

$$dE = Tds + Ydx + \mu dN \quad (\text{conserve energy})$$

$$\text{and } dE = \left(\frac{\partial E}{\partial T}\right)_x dT + \left(\frac{\partial E}{\partial X}\right)_T dX \quad (\text{material properties})$$

can be combined usefully.

More generally, can use any thermodynamic potential for this trick

3) I gave magnetic work  $dW = -\vec{H} \cdot d\vec{M}$

This is not trivial, or obvious

References: Callen  
Jackson

4) To get  $F(x, y)$  from  $dF = \left(\frac{\partial F}{\partial x}\right) dx + \left(\frac{\partial F}{\partial y}\right) dy$

I suggested method

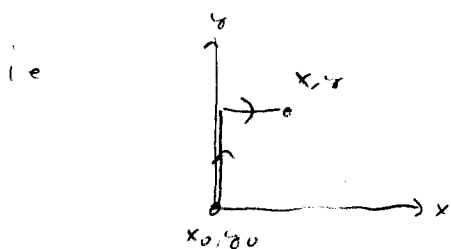
$$F(x, y) = \int \frac{\partial F}{\partial x} dx + K_1(y)$$

$$= \int \frac{\partial F}{\partial y} dy + K_2(x)$$

Usually this is easiest to do

Another way:

$$F(x, y) = \int_{(x_0, y_0)}^{(x, y)} dF + F(x_0, y_0) \quad \text{for any path}$$



$$F(x, y) = \int_{x_0, y_0}^{x, y} \frac{\partial F}{\partial y} dy + \int_{x_0, y}^{x, y} \frac{\partial F}{\partial x} dx + F_0$$

Might be easier to think about

5) Manipulating differentials:

$$\text{Given } dF = A dx + B dy$$

Can say many things:

$$\left(\frac{\partial F}{\partial x}\right)_y = A$$

(divide by  $dx$   
for  $dy=0$ )

$$\left(\frac{\partial F}{\partial y}\right)_A = A \left(\frac{\partial x}{\partial y}\right)_A + B$$

(divide by  $dy$   
at fixed  $A$ )

$$\left(\frac{\partial F}{\partial z}\right)_x = B \left(\frac{\partial y}{\partial z}\right)_x$$

(divide by  $dz$   
at  $dx=0$ )

$$\left(\frac{\partial F}{\partial x}\right)_z = A + B \left(\frac{\partial y}{\partial x}\right)_z$$

(divide by  $dx$   
at fixed  $z$ )

Can manipulate differentials as desired,  
as long as you are consistent in what  
is held constant

⇒ Equivalent to partial derivative relations  
I gave in lecture 1

$$\text{also } A \left(\frac{\partial x}{\partial y}\right)_F + B = 0$$

(divide by  $dy$   
at fixed  $F$ )