

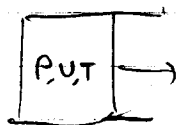
Lecture 4

Last time, introduced entropy $S = \int_{\text{rev}} \frac{dQ}{T} + \text{const}$

$$\text{or } dQ^{(\text{rev})} = T dS$$

Remark on $\int_{\text{irrev}} \frac{dQ}{T} < \int_{\text{rev}} \frac{dQ}{T} = \Delta S$

Consider isothermal expansion of ideal gas:



Irreversible: pull wall fast comp to molecular speeds

Then gas doesn't keep up, does not work

$\Rightarrow E = \text{const} \Rightarrow T = \text{const}$
for no heat input

Here $\int \frac{dQ}{T} = 0$

Compare to reversible: gas does work $w = \int P dV$
To keep T constant, need to add heat
to keep E constant.

So here $\int \frac{dQ}{T} > 0$

Either way, change in entropy is the same.

Want to talk more about energy.

One example of a thermodynamic potential

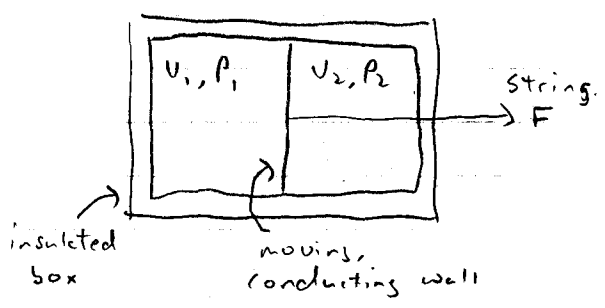
Explain...

Consider insulated ($ds=0$), closed ($dN=0$) system with fixed volume ($dV=0$)

Sounds like $dE = Tds - PdV + \mu dN = 0$

But can still change E if system has other degrees of freedom

For instance:



Reversibly pull string distance Δx
Do work

$$W = \int F dx \text{ on system}$$

V 's & P 's change, could work out, but know
 $\Delta E = W$
from 1st law

Later on, can move string back and recover W completely

Here F acts like a potential energy:
Can reversibly store & release work

(Compare to a spring)

Call energy stored this way "free" energy
 \Rightarrow available to do work.

Not all energy is free: if $P_1 = P_2$, no work available
 but $E \neq 0$

Can also see that equilibrium state has min possible E
 for given S, U, N

\Rightarrow any other state has free energy that can
 be converted to work (perhaps irreversibly)

So can find equil. by minimizing E (subject to constraints)
 \rightarrow Familiar from mechanics,

Several other thermodynamic potentials correspond
 to other constraints:

$$\text{Enthalpy } H = E - XY = ST + \mu N$$

$$dH = dE - XdY - YdX$$

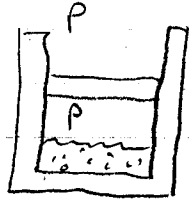
$$= TdS + YdX + \mu dN - XdY - YdX$$

$$\boxed{dH = TdS + XdY + \mu dN}$$

So $dH = 0$ for fixed S, Y, N

Can be used to store work under these conditions

Example:



Boiling liquid in piston,
in equil w/ vapor

Compress piston, convert gas \rightarrow liquid with fixed P
Do work on system

Expand piston, liquid \rightarrow gas, get work back

Show work stored is ΔH :

Compress piston by slightly increasing outside P

$$\text{Total work done } W = -(P + dP)\Delta V$$

$$= \Delta E \text{ of system}$$

But most of this work is done by environment,
goes back to environment in expansion

$$\text{Here free energy} = -dP \cdot \Delta V$$

$$= \Delta E + P\Delta V$$

$$= \Delta(E + PV)$$

$$= \Delta H, \text{ as claimed}$$

Here equilibrium determined as configuration that
minimizes H

\Rightarrow ie, fraction of liquid

Get derivative relations as before:

$$\text{Ex: } \left(\frac{\partial H}{\partial S}\right)_{N,Y} = T$$

Also Maxwell relations: $\left(\frac{\partial T}{\partial Y}\right)_S = -\left(\frac{\partial X}{\partial S}\right)_Y = -\frac{\partial^2 H}{\partial Y \partial S}$

(different from relations we got for E)

Other common thermodynamic potentials:

• Helmholtz free energy:

$$A = E - TS = XY + \mu N$$

$$dA = -SdT + YdX + \mu dN$$

Stores work at fixed (T, X, N)

Min at equilibrium at fixed (T, X, N)

• Gibbs free energy

$$G = E - TS - XY = \mu N$$

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

Store work min at eq, for fixed (T, Y, N)

• Grand potential

$$\Phi = E - TS - \mu N = XY$$

$$d\Phi = -SdT + YdX - Nd\mu$$

Store work, min at eq for fixed (T, X, μ)

Could make up others as needed... one for each combination of variables

Each has derivative relations,
can read off from differential form

$$\text{ie, } \Delta = - \left(\frac{\partial \Phi}{\partial \mu} \right)_{T, X}$$

Each also has set of three Maxwell relations
that don't explicitly involve potential

$$\text{ie, } \left(\frac{\partial S}{\partial X} \right)_{T, N} = - \left(\frac{\partial Y}{\partial T} \right)_{X, N} \quad \text{from } \frac{\partial^2 A}{\partial X \partial T}$$

These are useful, how to keep track?

All have generic form

Consider conjugate pairs $(X, Y)^{+}$ and (x, y)

Here let X include S and N (all extensive)
 Y include T and μ (all intensive)

Then Maxwell relations give

$$\left(\frac{\partial X}{\partial y} \right)_Y = \left(\frac{\partial x}{\partial Y} \right)_y \quad + \text{ for ext/int derive}$$

$$\text{and } \left(\frac{\partial X}{\partial x} \right)_Y = - \left(\frac{\partial y}{\partial Y} \right)_x \quad - \text{ for ext/ext, int/int derive}$$

Can hold any one variable from a third conjugate pair constant on both terms.

Example: $(T, S) + (P, V) \Rightarrow \boxed{\text{really } Y = -P !}$

$$\left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P \quad \text{and} \quad \left(\frac{\partial T}{\partial V} \right)_S = \left(\frac{\partial P}{\partial S} \right)_V$$

Can manipulate further using partial derivative relations from lecture 1

Why is this important?

Can only measure a few things experimentally
Use relations to get everything else

Response functions

What expts typically measure

Main example: heat capacity

Add heat to system ... temperature increases

Define $C = \frac{dQ}{dT}$

will differ depending on what is held fixed

$$C_x = \text{hold } X \text{ const} \quad C_y = \text{hold } Y \text{ const}$$

(almost always hold N const)

In general, $dQ = dE - YdX$

$$\text{So } C_x = \left(\frac{dQ}{dT} \right)_x = \left(\frac{\partial E}{\partial T} \right)_x$$

For C_y , note $dH = TdS - XdY = dQ - XdY$

$$\text{So } C_y = \left(\frac{\partial H}{\partial T} \right)_y$$

Useful to relate C_x & C_y :

$$\text{Use } \left(\frac{\partial Q}{\partial T}\right)_Y = \left(\frac{\partial Q}{\partial T}\right)_X + \left(\frac{\partial Q}{\partial x}\right)_T \left(\frac{\partial x}{\partial T}\right)_Y$$

\downarrow \downarrow $\overline{\partial x}$
 C_Y C_X

For $\left(\frac{\partial Q}{\partial x}\right)_T$, use $dQ = dE - Ydx$

$$\Rightarrow \left(\frac{\partial Q}{\partial x}\right)_T = \left(\frac{\partial E}{\partial x}\right)_T - Y$$

So

$$C_Y = C_X + \left[\left(\frac{\partial E}{\partial x}\right)_T - Y \right] \left(\frac{\partial x}{\partial T}\right)_Y$$

Some other useful relations:

$$dQ = Tds, \text{ so}$$

$$C_X = T \left(\frac{\partial S}{\partial T}\right)_X$$

$$C_Y = T \left(\frac{\partial S}{\partial T}\right)_Y$$

$$dA = -SdT + Ydx$$

$$\Rightarrow S = - \left(\frac{\partial A}{\partial T}\right)_X$$

$$\Rightarrow C_X = -T \left(\frac{\partial^2 A}{\partial T^2}\right)_X$$

while $dG = -SdT - XdY$

$$\Rightarrow S = - \left(\frac{\partial G}{\partial T}\right)_Y$$

$$\Rightarrow C_Y = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_Y$$

Example: ideal gas

$$E = \alpha N k_B T$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \alpha N k_B \quad - \text{measure to get } \alpha$$

$$C_P = C_V + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P$$

↓
0

↓

$$V = \frac{NkT}{P}$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{Nk}{P}$$

$$C_P = C_V + P \cdot \frac{Nk}{P}$$

$$C_P = (\alpha + 1) N k_B$$

Other important response functions

$$\text{Compressibility: } \chi_T = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{isothermal}$$

$$\chi_S = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad \text{adiabatic}$$

$$\text{Thermal expansion coefficient: } \alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Magnetic susceptibility

$$\chi_{T/S} = \left(\frac{\partial M}{\partial H} \right)_{T/S}$$