

## Chapter 5 + Section 1.6 (cont) → Free Energies

Enthalpy → energy plus the work to make room for the system under constant pressure from the environment

$$H \equiv U + PV \quad \leftarrow \text{total energy to create the system and put it into an environment}$$

But, the system can get its thermal energy from the surroundings, so all we really need to do is provide to the system any additional work

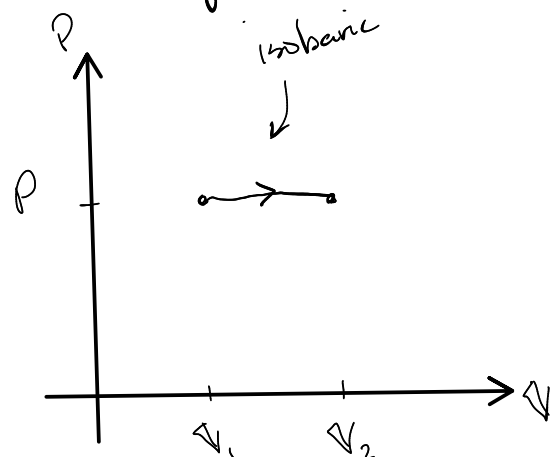
### Gibbs Free Energy

$$\begin{array}{l} G \equiv H - TS \\ G \equiv U + PV - TS \end{array} \quad \leftarrow \begin{array}{l} \text{energy to make the system and make} \\ \text{room for the system minus the heat} \\ \text{we get to extract from surroundings.} \end{array}$$

Helmholtz Free Energy → total energy to create the system minus the heat we can extract from the surroundings

$$F = U - TS$$

# Enthalpy



#1.34

$$W = -P(V_2 - V_1)$$

$$\Delta U = \frac{f}{2} N k_B \Delta T = \frac{f}{2} P \Delta V = \frac{f}{2} P(V_2 - V_1)$$

$$Q = \Delta U - W = \Delta U + P \Delta V$$

$$Q = \frac{f}{2} P(V_2 - V_1) + P(V_2 - V_1)$$

$$Q = \left(\frac{f}{2} + 1\right) P \Delta V$$

$$H \equiv U + PV$$

$$\Delta H = \Delta U + P \Delta V = Q$$

$$N k_B \Delta T = P \Delta V$$

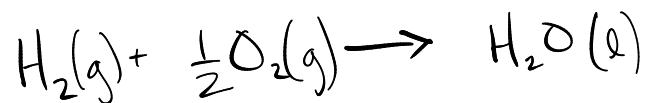
— or —

$$= \Delta P \cdot V$$

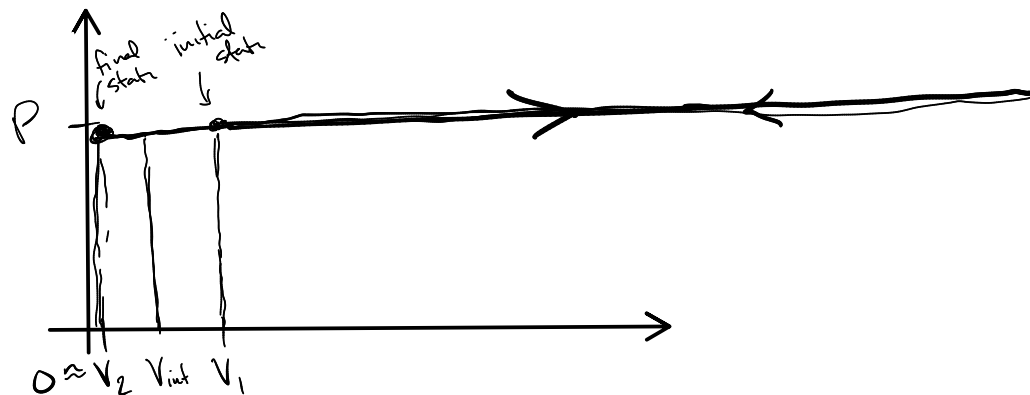
— but not —

$$= \underline{\underline{\Delta P \cdot \Delta V}}$$

Another example, what if we cause something to happen inside the tube & we measure the heat given off at constant pressure.



$$\Delta H = -286 \text{ kJ/mol}$$



1.4a)  $\frac{1 \text{ mol H}_2(\text{g})}{0.5 \text{ mol O}_2}$   
 $1.5 \text{ mol} \rightarrow n_m$

$$PV = n \cdot R \cdot T \leftarrow 298 \text{ K}$$

$\uparrow$        $\uparrow$        $\nwarrow$   
 $10^5 \text{ Pa}$      $1.5 \text{ mol}$      $8.31$

$1 \text{ mL} = 1 \text{ cm}^3$   
 $1000 \text{ L} = 1 \text{ m}^3$

$$V = \frac{nRT}{P} = \frac{1.5 \cdot 8.31 \cdot 298}{10^5} = 0.037 \text{ m}^3 = 37 \text{ L}$$

$n_m$  after the reaction?

$$V_{\text{int}} = \frac{1 \cdot 8.31 \cdot 298}{10^5} = 0.0248 \text{ m}^3$$

↓ this condenses  
to give ~ 0 L  
of liquid, giving  
up heat along the way

$$V = \frac{nRT}{P} \xrightarrow{\text{constant}} V \propto n \rightarrow \frac{V_{\text{int}}}{V_1} = \frac{n_2}{n_1} = \frac{1}{1.5}$$

$$V_{\text{int}} = 0.0248 \text{ m}^3$$

So what total work has been done?

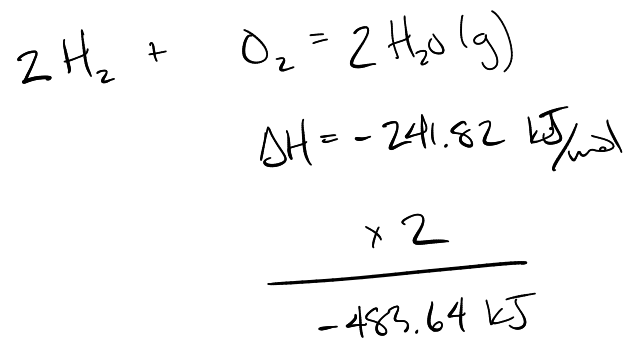
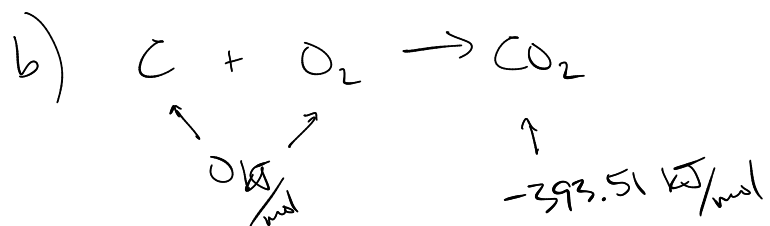
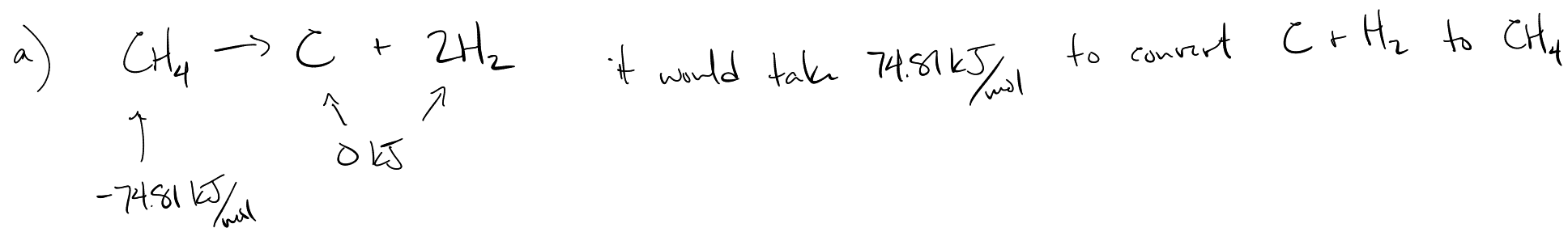
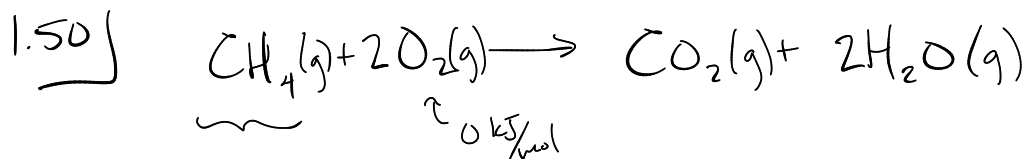
$$W = - \int_{0.037 \text{ m}^3}^{0 \text{ m}^3} P dV = -10^5 \text{ Pa} (0 - 0.037 \text{ m}^3)$$

$$= 3700 \text{ J} = 3.7 \text{ kJ}$$

$$\rightarrow \Delta H = -286 \text{ kJ} = \Delta U - W$$

$$-286 \text{ kJ} = \Delta U - 3.7 \text{ kJ}$$

$$\boxed{\Delta U = -282.3 \text{ kJ}}$$



c)  $\Delta H_{\text{reaction}} = 74.81 - 393.51 \text{ kJ/mol} - 483.64 \text{ kJ}$

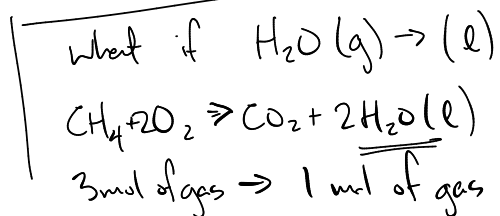
$\Delta H_{\text{reaction}} = -802.34 \text{ kJ} \rightarrow$  heat given to the surroundings

d)  $802.34 \text{ kJ}$

e)  $\Delta H = U + p\Delta V$   
 Arrows point to  $U$  and  $p\Delta V$  with "find this" written next to the arrow pointing to  $p\Delta V$ .

$\Delta H = U$  when final mixture is a gas

$pV = nRT \rightarrow p\Delta V = \Delta n R \cdot T$   
 $= 0 \text{ mol} \cdot 8.31 \cdot 298 \text{ K}$



$p\Delta V = -2 \text{ mol} \cdot 8.31 \cdot 298 \text{ K}$   
 $= -4.9 \text{ kJ}$

$$\Delta H_{\text{reaction}} = ?$$

f) ?

also do 1.55

## Gibbs Free Energy

$$G = U + PV - TS$$

$$G = H - TS$$

$$dG = dU - TdS + pdV$$

$$dG = \pm Q + \pm W - TdS + pdV$$

- for a reversible process  
(no new entropy is created)

- $\pm Q_{\text{rev}} = TdS$

- $\pm W = -pdV + \pm W_{\text{other}}$   
↳ electrical

$$dG = \cancel{TdS} - \cancel{pdV} + \pm W_{\text{other}} - \cancel{TdS} + \cancel{pdV}$$

$$dG = \pm W_{\text{other}}$$

not reversible

$$dG \leq \pm W_{\text{other}} \text{ at constant } T, p$$

## Thermodynamic Potentials

$$dF = dU - TdS$$

$$dF = \pm Q + \pm W - TdS$$

for a reversible process  
(no new entropy is created)

$$\pm Q_{\text{rev}} = TdS$$

$$dF = TdS + \pm W - TdS$$

$$dF = \pm W$$

↳ amount of work done  
on the system by  
you or by surroundings

otherwise, (not a reversible process)

$$dF \leq \pm W$$

How is  $\Delta G_f$  measured?

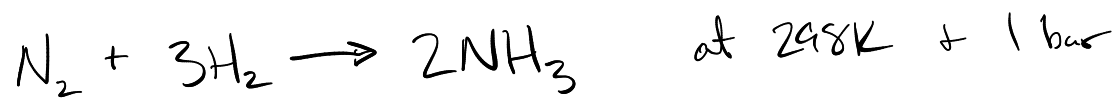
First measure  $\Delta H \rightarrow$  heat absorbed or released for a reaction at constant pressure & no other work has been done

Then calculate  $\Delta S$  from initial & final states using heat capacity data

$$\Delta S = \int_0^{T_f} \frac{C_p}{T} dT$$

$$\Delta G = \Delta H - T\Delta S$$

So lets do an example: (5.2)



$$\downarrow$$
$$\Delta H = 0 \text{ kJ}$$

$$S = 191.61 \text{ J/K mol}$$

$$\downarrow$$
$$\Delta H = 0 \text{ kJ}$$

$$S = 130.68 \text{ J/K mol}$$

$$\rightarrow \Delta H = -46.11 \text{ kJ}$$

$$S = 192.45 \text{ J/K mol}$$

$$\Delta H = 2 \text{ mol} \cdot (-46.11 \text{ kJ/mol}) = -92.22 \text{ kJ}$$

$$\Delta S = S_f - S_i = 2 \cdot 192.45 \text{ J/K mol} - 3(130.68) - 191.61$$
$$= -198.75 \text{ J/K}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{watch out for kJ!}$$

$$= -92.22 \text{ kJ} - 298(-0.19875 \text{ kJ/K})$$

$$\underline{\underline{\Delta G = -32.99 \text{ kJ}}}$$

compare!

from the book

$$\Delta G = -16.45 \text{ kJ/mol}$$

for this reaction

$$\Delta G = 2 \text{ mol} \cdot (-16.45 \text{ kJ/mol}) = \underline{\underline{-32.9 \text{ kJ}}}$$

## Electrolysis, Fuel Cells, Batteries (another example)



↑ electrical work must be done

$$\Delta H = \underline{286 \text{ kJ}} \rightarrow \text{heat out when we run in reverse}$$

To run this reaction forward we need to put in 286 kJ of energy

→ some of this will push aside the atmosphere

$$p\Delta V = \Delta n RT = 1.5 \text{ mol} \cdot (8.31 \text{ J/mol K})(298 \text{ K}) = 3714 \text{ J}$$

↑ gas form

$$= 3.7 \text{ kJ}$$

→ so, 282 kJ will remain in the system in the form of potential energy in the chemical bonds  $\sim 4 \text{ kJ}$



Do we need to do all of this work, or can we get some help from surroundings?

What is the change in entropy?

$$S_{H_2O} = 70 \text{ J/K}$$

$$S_{H_2} = 131 \text{ J/K}$$

$$S_{O_2} = 205 \text{ J/K}$$

← from the back of the book

products

$$S_{\text{prod}} = 131 \text{ J/K} + \frac{1}{2} (205 \text{ J/K}) = 233.5 \text{ J/K}$$

$$\Delta S = S_p - S_r = 233.5 \text{ J/K} - 70 \text{ J/K} = 163.5 \text{ J/K}$$

entropy increased

$$dQ \leq T dS$$

$$Q = T \Delta S = 298 \text{ K} \cdot 163.5 \text{ J/K}$$

$$Q = \underline{48.7 \text{ kJ}}$$

So of the 286 kJ that go in, 48.7 kJ can come from heat from surroundings

$$286 \text{ kJ} - 48.7 \text{ kJ} = \underline{\underline{237.3 \text{ kJ}}} \rightarrow \text{come from } \underline{\underline{\text{electrical work}}}$$

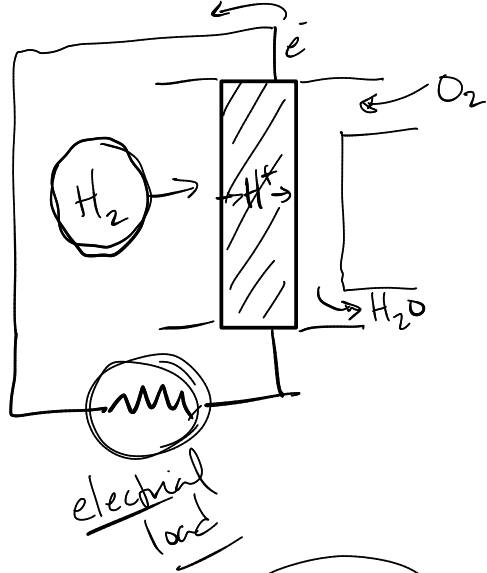
$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G_{H_2O} = -228.57 \text{ kJ} \quad \Delta G_{H_2} = 0 \text{ kJ} \quad \Delta G = 0 \text{ kJ}$$

## HW 5.1 + 5.5

$$\Delta G = \Delta G_{\text{prod}} - \Delta G_{\text{react}} = 0 - 228.57 \\ = \underline{\underline{228.57 \text{ kJ}}}$$

In reverse, we can extract 237 kJ of electrical work



gray H<sub>2</sub>    blue H<sub>2</sub>    green H<sub>2</sub>  
↳ sdar

→ 49 kJ of waste heat goes to the environment

→  $\Delta U = 282 \text{ kJ}$  → comes from chemical reactions

→  $P\Delta V = 4 \text{ kJ}$  → comes from the collapse of gas to liquid

$$\text{efficiency} = \frac{\text{get}}{\text{pay for}}$$

Fuel cell

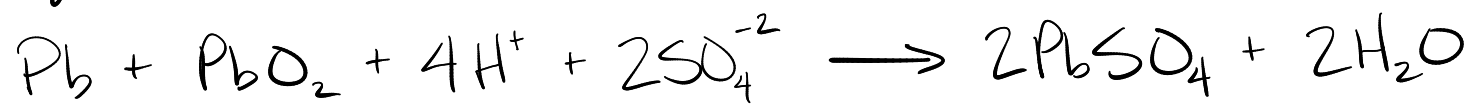
$$\frac{237 \text{ kJ}}{286 \text{ kJ}} = \underline{\underline{83\%}}$$

compare to efficiencies  
we would have  
gotten in chapter 4

max theoretical  
engine efficiency → 66%

max theoretical car  
engine efficiency → 50%  
↳ practically → 20-30%

# Battery



start w/  $\Delta H = -316 \text{ kJ/mol}$

↑ energy out from reaction at constant pressure

what about  $\Delta G = -394 \text{ kJ/mol}$

↑ electrical energy out

$\Delta G$  is more than the  $\Delta H$ . How? Heat is coming in to the system from surroundings!

How much?

$$394 \text{ kJ/mol} - 316 \text{ kJ/mol} = 78 \text{ kJ/mol}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G - \Delta H = -T\Delta S$$

$$-394 - (-316) = -298 \Delta S$$

$$\Delta S > 0$$

$$78 \text{ kJ/mol} = T\Delta S$$

increase in entropy

means the heat is being absorbed from surroundings

$$\Delta S = \frac{78 \text{ kJ}}{298 \text{ K}} = 261.7 \frac{\text{J}}{\text{K}}$$

watch out for units

Energy / charge  $\rightarrow$  potential (voltage)

$$\text{voltage} = \frac{\Delta W_E}{q} = \frac{394 \text{ kJ}}{2e \cdot N_A \cdot 1.6 \cdot 10^{-19} \frac{\text{C}}{e}} = 2.84 \text{ V} \quad \leftarrow \begin{array}{l} \text{per "cell" in a car battery} \\ 6 \text{ "cells"} \rightarrow \underline{12\text{V}} \end{array}$$

$\uparrow$   
need to know how many electrons  
are moved during the reaction  
 $2e^-$

Thermodynamic identity

$$dU = T dS - P dV + \mu dN$$

but what about  $H, F, G$ ? How do these change when conditions change?

$$\rightarrow H = U + pV$$

$$dH = dU + p dV + V dp$$

$$\hookrightarrow T dS - p dV + \mu dN + p dV + V dp$$

$$dH = T dS + V dp + \mu dN$$

$\rightarrow$  So the variables have changed from  $dU$   
we tend to use enthalpy

when  $dp = 0$

$dN = 0$

$dH = T dS \leftarrow$  heat at constant pressure

What about  $F$ ?

$$\rightarrow F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dF = -S\underline{dT} - p\underline{dV} + \mu\underline{dN}$$

What about  $G$ ?  $\rightarrow$  you derive this

We can use these identities to derive many useful statements.

Ex:  $dF = -SdT - pdV + \mu dN$

hold  $V + N$  constant  $\rightarrow dV + dN$  are 0

$$dF = -SdT$$

$$S = -\left(\frac{dF}{dT}\right)_{V,N}$$

$\leftarrow$  what does this mean?  
entropy is the rate of change of  $F$  w.r.t.  $T$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

What about Gibbs?

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad \underline{\underline{V = \left(\frac{\partial G}{\partial P}\right)_{T,N}}}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

How does the Gibbs Free Energy change w/ pressure

Use reference data  $\rightarrow$  1 mol of C (graphite)  $\Rightarrow 5.3 \cdot 10^{-6} \text{ m}^3$

$\Delta G_{\text{C}} = 0 \text{ kJ} \leftarrow$  most stable form

Gibbs will increase by  $5.3 \cdot 10^{-6} \text{ J}$  for each additional Pa of pressure above atmospheric pressure

Ex: 1 mol of  $\text{H}_2\text{O}(\text{l})$  at  $25^\circ\text{C}$  (298K)

Gibbs at  $30^\circ\text{C}$ ? (303K) -

$G_{\text{H}_2\text{O}} = -237.13 \text{ kJ}$  at 298K and 1 atm

$$S = \left(\frac{\partial G}{\partial T}\right)_{P,N}$$

$$S_{\text{H}_2\text{O}} = 69.91 \text{ J/K}$$

$$\Delta G = S \cdot \Delta T$$

$$= 69.91 \cdot 5 \text{ K} = 349.55 \text{ J}$$

$$+ \underline{-237.13 \text{ kJ}} \quad \underline{-236.78 \text{ kJ}}$$

units warning!



new  
Gibbs  
 $\downarrow$

5.14 → Monday

Now do 5.12 then come back to 5.14.

Thermodynamic identity

$$dU = \underline{T} dS - \underline{P} dV + \underline{\mu} dN$$

$$dU = \left[ \frac{\partial U}{\partial S} \right] dS + \left[ \frac{\partial U}{\partial V} \right] dV + \frac{\partial U}{\partial N} dN$$

$$\frac{\partial U}{\partial S} = T$$

$$\frac{\partial U}{\partial V} = -P$$

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) = \left( \frac{\partial T}{\partial V} \right)_S$$

$$\frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right) = - \left( \frac{\partial P}{\partial S} \right)_V$$

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

$$dS(U, V, N) = \underbrace{\left( \frac{\partial S}{\partial U} \right)_{U, V}}_{\frac{1}{T}} dU + \underbrace{\left( \frac{\partial S}{\partial V} \right)_{U, N}}_{\frac{P}{T}} dV + \underbrace{\left( \frac{\partial S}{\partial N} \right)_{U, V}}_{-\frac{\mu}{T}} dN$$

$$T dS = dU + P dV - \mu dN$$

$$f(x, y)$$

$$\left( \frac{\partial f}{\partial x} \right)_y$$

$$\left( \frac{\partial f}{\partial y} \right)_x$$

$$\frac{\partial^2 f}{\partial x \partial y}$$

Now do for Gibbs

$$dG = dU + p dV - T dS \quad (dN = 0)$$

$$dG = \frac{\partial G}{\partial U} dU + \frac{\partial G}{\partial V} dV + \frac{\partial G}{\partial S} dS$$

$$\frac{\partial}{\partial S} \left( \frac{\partial G}{\partial V} \right) = \frac{\partial}{\partial V} \left( \frac{\partial G}{\partial S} \right)$$

$$\left( \frac{\partial p}{\partial S} \right)_V = - \left( \frac{\partial T}{\partial V} \right)_S$$

Now for Helmholtz + Enthalpy then back to 5.14...



## 5.2 / Free Energy as a

Force toward Equilibrium

$$dS_{\text{total}} = dS + dS_R$$

rewrite in  
terms of system's  
variables

$$dS_R = \frac{1}{T} dU_R + \frac{P}{T} dV_R + \frac{\mu}{T} dN_R$$

$$dV_R = 0$$

$$dN = 0$$

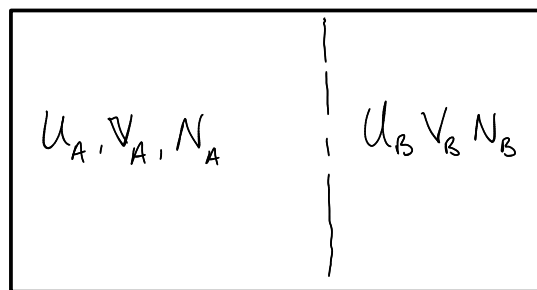
$$dU = -dU_R \leftarrow \text{energy is conserved}$$

$$dS_{\text{total}} = dS_{\frac{T}{T}} - \frac{1}{T} dU$$

$$= \frac{1}{T} (T dS - dU)$$

$$= -\frac{1}{T} (dU - T dS)$$

Helmholtz!  $dF$



surrounding  
(reservoir)

$$dS_{\text{total}} = -\frac{dF}{T}$$

↑ increase this

↓ decrease that

Conditions

$$dT = 0$$

$$dV = 0$$

$$dN = 0$$

So, the system will minimize  
its Helmholtz free energy

What about keeping Pressure, temperature and number constant and letting  $V$  change?

$$dS_{\text{total}} = dS + dS_{\text{res}}$$

$$\hookrightarrow dS_{\text{res}} = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \rightarrow 0$$

$$dS_{\text{res}} = -dS$$

$$dS_{\text{total}} = dS - \frac{1}{T} dU - \frac{P}{T} dV$$
$$= -\frac{1}{T} (dU - T dS + P dV)$$

$\Delta$  Gibbs free energy  $\rightarrow dG$

Conditions:

$$dT = 0$$

$$dp = 0$$

$$dN = 0$$

$$dS_{\text{total}} = -\frac{dG}{T}$$

system will spontaneously minimize Gibbs

At constant energy & volume,  $S$  tends to increase

At constant temperature & volume,  $F$  tends to decrease.

At constant temperature & pressure,  $G$  tends to decrease

Is this intuitive from their definitions

$$G = U + PV - TS$$

$\downarrow \quad \downarrow \quad \uparrow$

Derive chemical potential for an ideal gas, as a function of pressure

$$\mu = \frac{G}{N} \leftarrow \text{find this}$$

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P}$$

$$\frac{\partial \mu}{\partial p} = \frac{1}{N} \frac{\partial G}{\partial p}$$

$$\left( \frac{\partial G}{\partial p} \right)_{T,N} = V$$

$$\frac{\partial \mu}{\partial p} = \frac{1}{N} V$$

$$\text{ideal gas} \rightarrow \frac{V}{N} = \frac{k_B T}{p}$$

$$\frac{\partial \mu}{\partial p} \Rightarrow \frac{k_B T}{p}$$

reference point

another reference

$$\int d\mu = \int \frac{k_B T}{p} dp \Rightarrow \mu(T, p) - \mu^\circ(T) = \underbrace{k_B T \ln p - k_B T \ln p^\circ}_{=}$$

$$\Delta \mu = k_B T \ln \frac{p}{p^\circ}$$

$$\mu(T, p) = k_B T \ln \left( \frac{p}{p^\circ} \right) + \mu^\circ(T)$$

We already have an expression for  $\mu(T, P)$  from chapter 3.5 notes  
(problem 5.22)

$$\mu = -k_B T \ln \left[ \frac{V}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right]$$

$$\mu = -k_B T \ln \left( \frac{V}{N} \right) - \frac{3}{2} k_B T \ln \left( \frac{2\pi m k_B T}{h^2} \right)$$

$$\uparrow \frac{k_B T}{P}$$

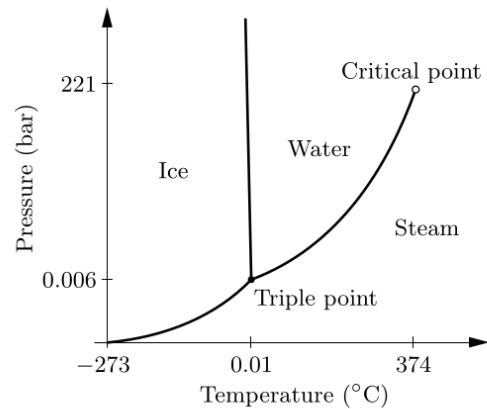
$$\mu = -k_B T \ln \left( \frac{k_B T}{P} \right) - \frac{3}{2} k_B T \ln \left( \frac{2\pi m k_B T}{h^2} \right)$$

$$\mu = k_B T \ln \left( \frac{P}{k_B T} \right) - \frac{3}{2} k_B T \ln \left( \frac{2\pi m k_B T}{h^2} \right)$$

does this  
mean the  
 $P^0$  is  $k_B T$ ?

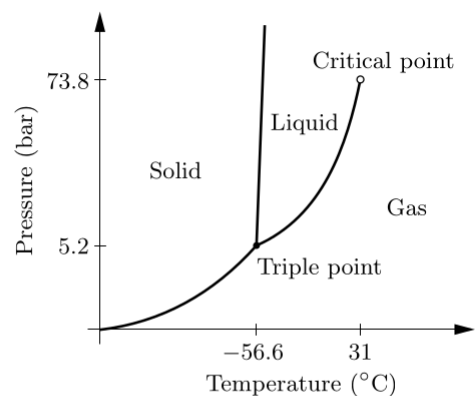
only a function of  $T = \mu^0(T)$  (monatomic ideal gas)

5.3



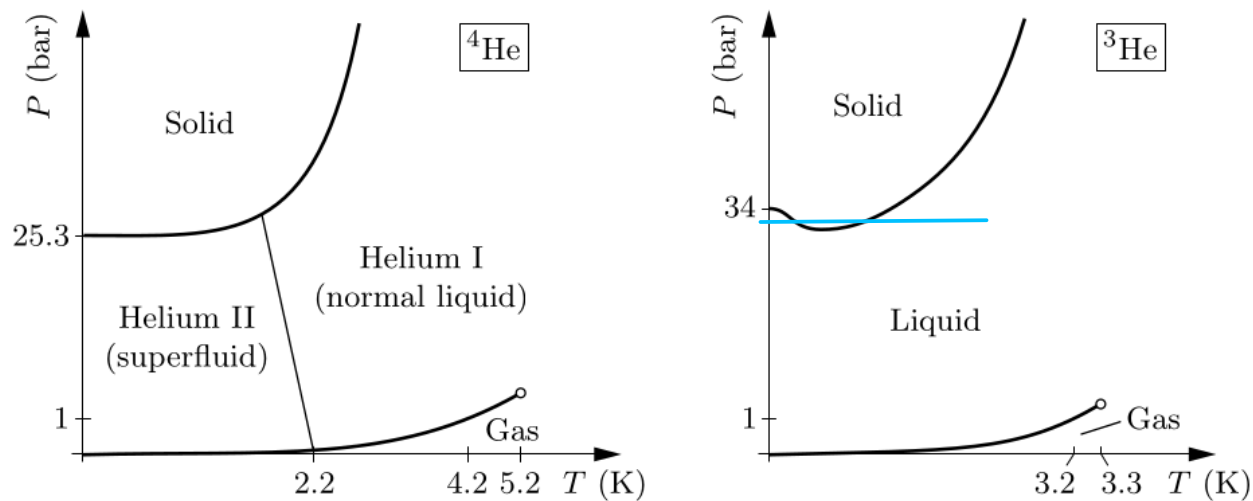
$T$ (°C)	$P_v$ (bar)	$L$ (kJ/mol)
-40	0.00013	51.16
-20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

**Figure 5.11.** Phase diagram for H<sub>2</sub>O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).

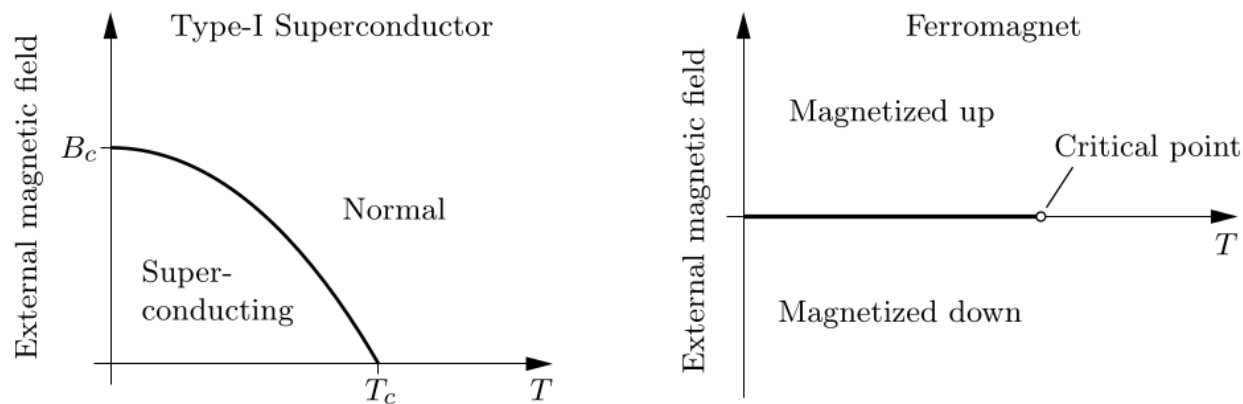


$T$ (°C)	$P_v$ (bar)
-120	0.0124
-100	0.135
-80	0.889
-78.6	1.000
-60	4.11
-56.6	5.18
-40	10.07
-20	19.72
0	34.85
20	57.2
31	73.8

**Figure 5.12.** Phase diagram for carbon dioxide (not to scale). The table gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Data from Lide (1994) and Reynolds (1979).



**Figure 5.13.** Phase diagrams of  $^4\text{He}$  (left) and  $^3\text{He}$  (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of  $^3\text{He}$  below 3 mK.



**Figure 5.14.** Left: Phase diagram for a typical type-I superconductor. For lead,  $T_c = 7.2$  K and  $B_c = 0.08$  T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis.

































