Announcements

1. Exam 1 Solutions are posted
2. Homework # 2 was posted Wed afternoon; is due next Friday
3. Distribution of scores: 98, 98, 98, 98, 98, 97, 97, 96 , 96 , 96, 88, 81, 80, 79,78, ...

NOT grading on curve: All A's or all B's is possible

Last year's grades:

Score	Grade
90-100	A
86-89	A-
81-85	B+
75-80	B
70-74	B-
68-70	C+
63-67	C
60-62	C-
50-69	D

The FUNDAMENTAL EQUATION combines 1st and 2nd Laws

$\Delta U = q + w$ (always true for CLOSED system

$dU = dq + dw = dq_{rev} + dw_{rev}$, because U is state function

but $dS = dq_{rev} / T$ which gives **$dq_{rev} = T\,dS$**

and $dw_{rev} = -pdV$ (because $p=p_{ext}$ if $dw_{useful} = 0$)

$dU = T\,dS - pdV$ = **"The Fundamental Equation"**

Why calculus? $\Delta U = T\,\Delta S - p\,\Delta V$ only if T and P constant. But no such restrictions for dU

U is U(S,V) (and also U = U(T,V) = U(P,T) = etc.

What is the S slope of U (if V is constant) ? **T**

Therefore : $\left(\frac{\partial U}{\partial S}\right)_V = T$

What is the V slope of U (if S is constant)? **-p**

And : $\left(\frac{\partial U}{\partial V}\right)_S = -p$

How is G affected by temperature and pressure?

$G = H - TS = U + pV - TS$ (by definition)

$dG = dU + d(pV) - d(TS)$ by def.

$= T\,dS - p\,dV + p\,dV + V\,dp - T\,dS - S\,dT$

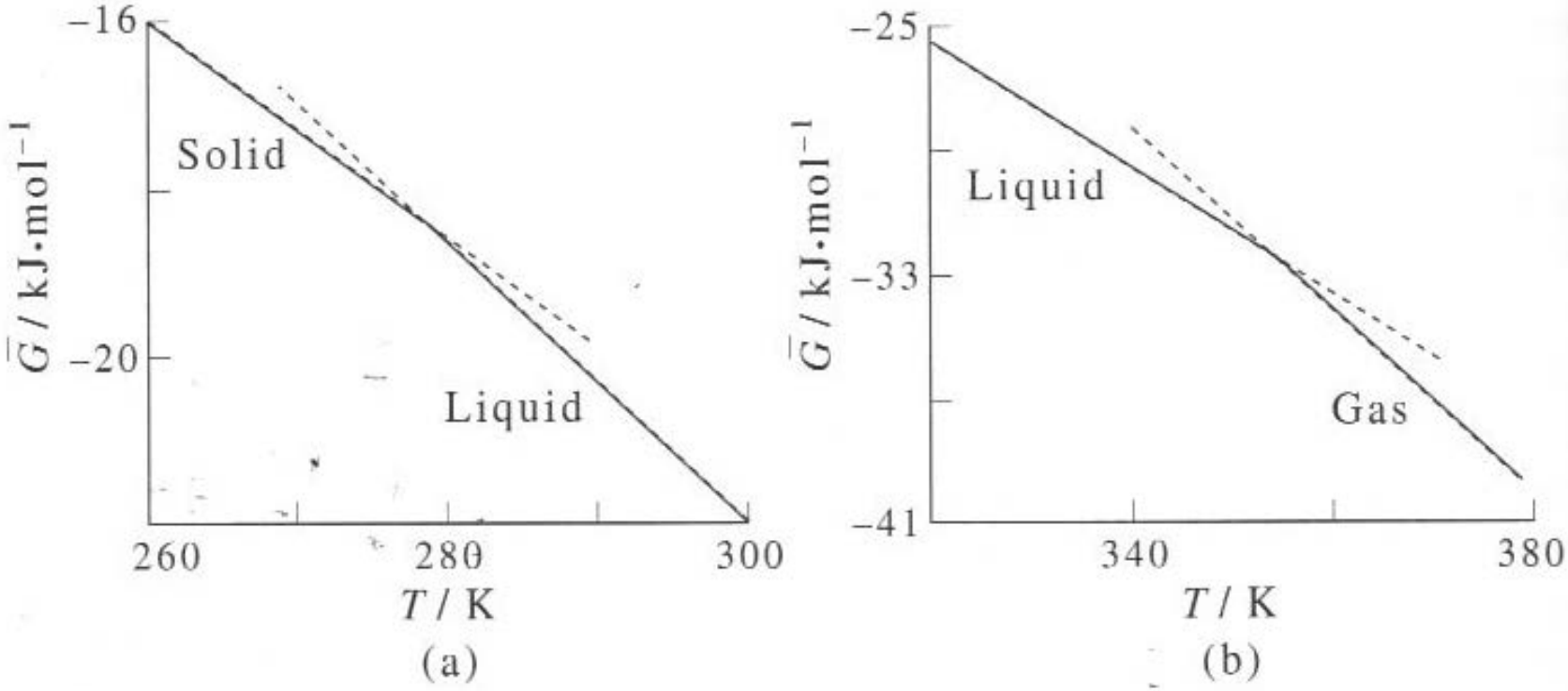
$dG = V\,dp - S\,dT$

T Slope = -S (the more ***ordered*** phase has a ***less negative*** T slope)

p Slope = V (the ***larger*** phase has **larger** p slope)

dG = Vdp – SdT for Benzene

T Slope = -S (more ***ordered*** phase has ***less negative*** slope)



A plot of $\overline{G}(T)$ versus T for benzene in the region around (a) its melting point (279 K) and (b) its boiling point (353 K).

TEMPERATURE DEPENDENCE OF ΔG

$dG = VdP - SdT + w^*$

w^* is w_{useful}

at const. P $\quad dG = -SdT$ & $w^* = 0$

$$\Delta G = -\int_{T_1}^{T_2} S\,dT \cong -S\Delta T$$

at a given T $\quad \Delta G = \Delta H - T\Delta S$

at equilibrium $\quad \Delta G = 0$ if $T = T_{eq}$

so $(\Delta H = T_{eq}\Delta S)$ equil.

(FORCE VS ORDER)

Assuming ΔH & ΔS ~ const.

if $\Delta H = +$ & $\Delta S = +$ $\quad \Delta G = +$ at low T

$\Delta G = -$ at high T

example: evaporation

spontaneous at High T

if $\Delta H = -$ & $\Delta S = -$ $\quad \Delta G = -$ at low T

$\Delta G = +$ at high T

example Condensation

spontaneous at LOW T

if ΔH is $-$ & $\Delta S = +$ ALWAYS SPONTANEOUS

EXAMPLE: BURNING COAL & OIL

Temperature Dependence of ΔG (qualitatively)

$G = H - TS$

$\Delta G = \Delta H - T\,\Delta S$ at a given T ; recall $\Delta H = q = -T\,\Delta S_{surr}$

At equilibrium $\Delta G = 0$; $= -T\,\Delta S_{surr} \quad -T\,\Delta S$

so $\Delta H = T_{eq}\,\Delta S$ at equilibrium

if ΔH and ΔS are approximately CONSTANT

4 cases: 1) $\Delta H = +$ (endothermic) , $\Delta S = +$ (disordering)

ΔG is negative at high T, positive at low T

Example ? Evaporation

2) $\Delta H = -$ (exothermic) , $\Delta S = -$ (ordering)

Example ? Condensation

PRESSURE DEPENDENCE

L3

03: 14-1

AT Const T

$$dG = V\,dP$$

$$\Delta G = \int_{P_1}^{P_2} V\,dP \cong V\Delta P$$ **if V is constant**

$$= n\bar{V}(P_2 - P_1)$$

Make diamond from graphite

$$C(gr) \longrightarrow C\ dia$$

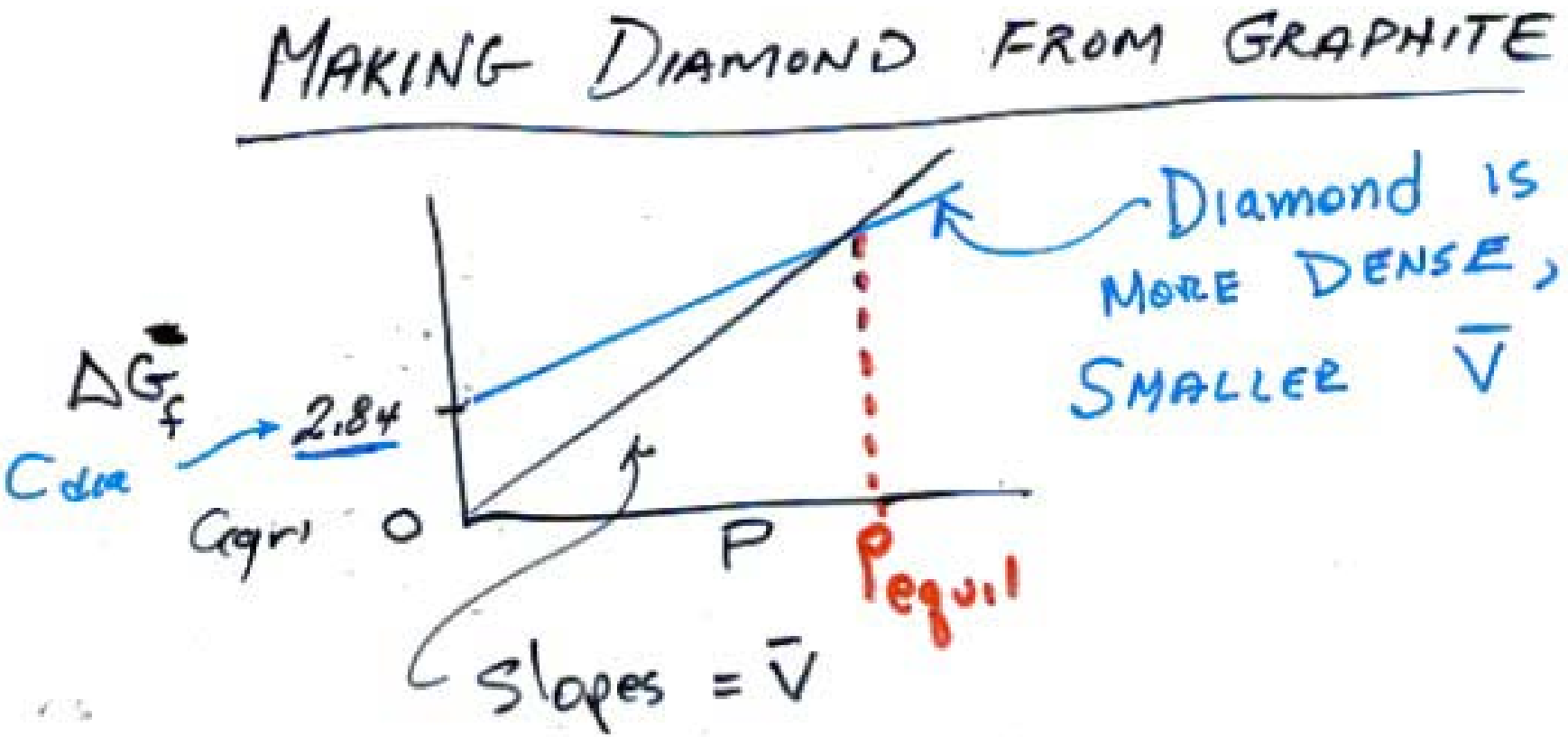
at 1atm $\quad \Delta G^\circ = \Delta G_f^\circ(dia) - \Delta G_f^\circ(gr)$

$$= +2.84\ kJ - 0$$

in useful words, **diamond ---> charcoal is a spontaneous process**

$dG = Vdp - SdT$

p Slope = V (the ***larger volume*** i.e., ***less dense*** phase has the ***largest slope*** in a G vs. p plot)

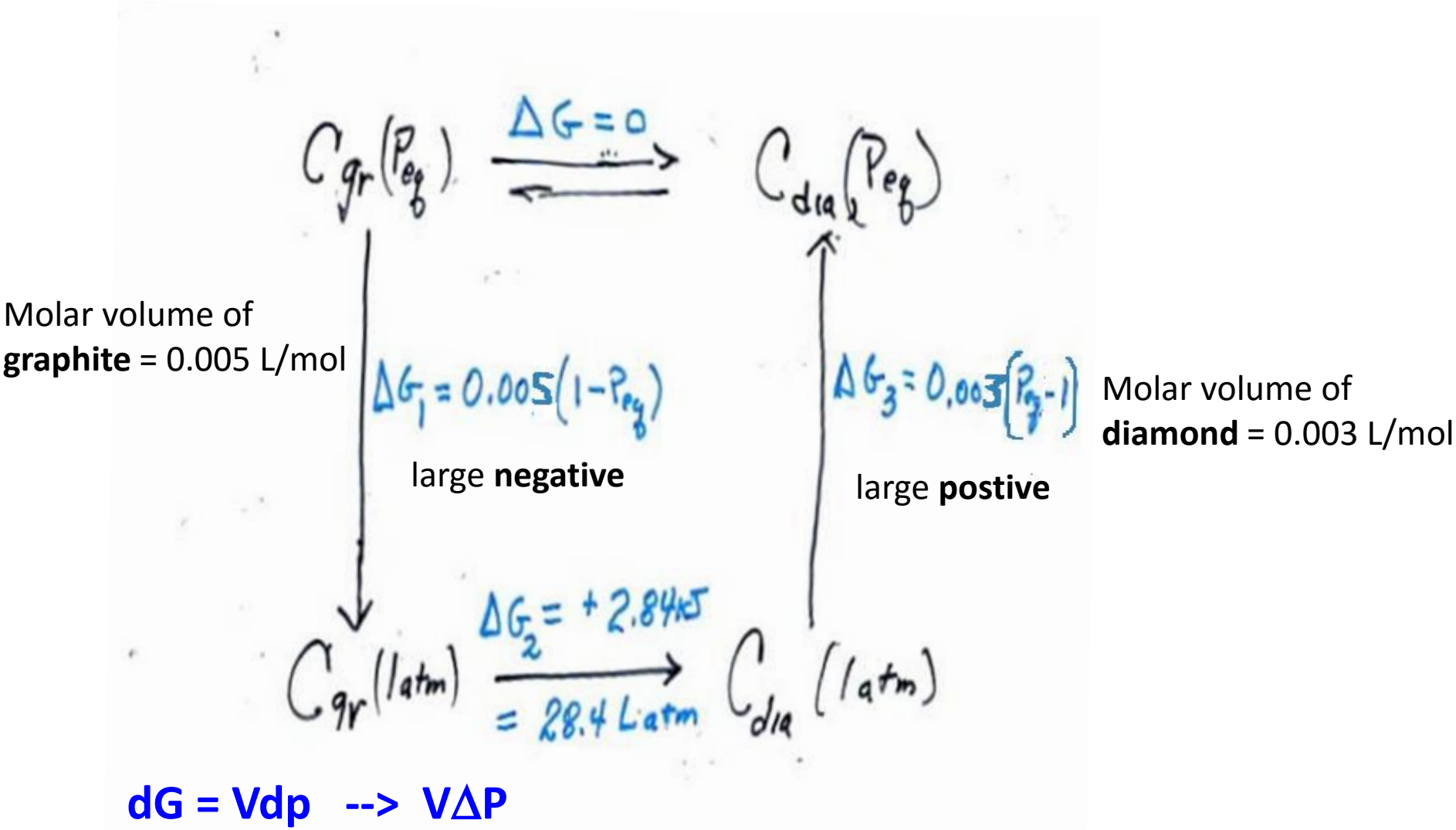


Molar volume of **graphite** = 0.005 L/mol

density = 2.25 gcm-1

Molar volume of **diamond** = 0.003 L/mol

density = 3.4 gcm-1



dG = Vdp --> VΔP

-28.4 Latm needed= - 0.002Lmol^{-1} x P_{eq}

-28.4 Latm mol^{-1}/ -0.002Lmol^{-1} =P_{eq} = 14,000 atm