Solutions to Problem Set 5

1. ideal gas, 1 mol 1 L 25 °C → 100 L 25 °C

Equation	Basis for the equation	Eq. #
$d\mathbf{U} = (\partial\mathbf{U}/\partial T)_V dT + (\partial\mathbf{U}/\partial V)_T dV$	$\mathbf{U} = \mathbf{U}(T,V)$	1
$d\mathbf{H} = (\partial\mathbf{H}/\partial T)_p dT + (\partial\mathbf{H}/\partial p)_T dp$	$\mathbf{H} = \mathbf{H}(T,p)$	2
$\Delta\mathbf{U} = 0$ **Answer** $\Delta\mathbf{H} = 0$ **Answer**	For an ideal gas, $(\partial\mathbf{U}/\partial V)_T = 0$ and $(\partial\mathbf{H}/\partial p)_T = 0$ and $dT = 0$ for this problem	3 4
$d\mathbf{S} = (\partial\mathbf{S}/\partial T)_V dT + (\partial\mathbf{S}/\partial V)_T dV$	$\mathbf{S} = \mathbf{S}(T,V)$	5
$(\partial\mathbf{S}/\partial V)_T = (\partial p/\partial T)_V$	Derived (see lecture notes Part 4) starting from $d\boldsymbol{U} = \eth q_{rev} - p dV = T d\boldsymbol{S} - p dV$ and use of cross derivatives	6
$p = RT/V$ $(\partial p/\partial T)_V = R/V$ $(\partial\mathbf{S}/\partial V)_T = R/V$	Ideal gas equation of state for one mol Differentiating Substituting Eq 8 into Eq 6	7 8 9
$\Delta\mathbf{S} = \int (R/V) dV$	Substituting Eq 9 into Eq 5 and using $dT = 0$ for this problem	10
$\Delta\mathbf{S} = R \ln(V_f/V_i)$ $= (1 \text{ mol})(8.314 \text{ J mol}^{-1}\text{K}^{-1})\bullet$ $\ln(100/1) = 38.3 \text{ J K}^{-1}$ **Answer**	Integrating Eq 10 between the limits	11
$\mathbf{A} = \mathbf{U} - T\mathbf{S}$	Definition	12
$\Delta\mathbf{A} = \Delta\mathbf{U} - T\Delta\mathbf{S}$	At constant T	13
$\Delta\mathbf{A} = 0 - (298)(38.3 \text{ J K}^{-1})$ $\Delta\mathbf{A} = -11409. \text{ J}$	From $\Delta\mathbf{U} = 0$ Eq 3 & $\Delta\mathbf{S}$ from Eq 11, and given T= 298 K	14
$\mathbf{G} = \mathbf{H} - T\mathbf{S}$	Definition	12
$\Delta\mathbf{G} = \Delta\mathbf{H} - T\Delta\mathbf{S}$	At constant T	13
$\Delta\mathbf{G} = 0 - (298)(38.3 \text{ J K}^{-1})$ $\Delta\mathbf{G} = -11409. \text{ J}$	From $\Delta\mathbf{H} = 0$ Eq 4 & $\Delta\mathbf{S}$ from Eq 11, and given T= 298 K	14

2. (a) ideal gas, 1 mol 22.4 L, 0 °C → 224 L, 0 °C isothermal, reversible

Equation	Basis for the equation	Eq. #
$\Delta\mathbf{U} = 0$ **Answer** $\Delta\mathbf{H} = 0$ **Answer** $\Delta\mathbf{S} = R \ln(V_f/V_i)$ $= (1 \text{ mol})(8.314 \text{ J mol}^{-1}\text{K}^{-1})\bullet$ $\ln(224/22.4) = 19.14 \text{ J K}^{-1}$ **Answer** $\Delta\mathbf{A} = -(273)(19.1 \text{ J K}^{-1})$ $= -5226 \text{ J}$ **Answer** $\Delta\mathbf{G} = -(273)(19.1 \text{ J K}^{-1})$ $= -5226 \text{ J}$ **Answer**	Using all the same equations as in problem 1 (Eq 1-14) except for $V_f = 224$ L and $V_i = 22.4$ L, T = 273 K Reversible or otherwise, the same equations hold for state functions for isothermal process for ideal gas.	

$\delta W = - p_{op} dV$	Definition of pV work	1
$p_{op} = p_{gas}$ $p_{gas} = (1)RT/V$	reversible ideal gas equation of state, 1 mole	2 3
$\delta W = - RTdV/V$ $W = - \int RTdV/V = - (1 \text{ mol})(8.314 \text{ J mol}^{-1}\text{K}^{-1})273 \bullet \ln(224/22.4)$ $= - 5226$ J **Answer**	From Eq 1, 2 and 3 Integrating	4
$d\mathbf{U} = \delta q + \delta W$	First Law of Thermodynamics	5
$\Delta\mathbf{U} = 0$	Already found	
$0 = q + W$ $q = -W = + 5226$ J **Answer**	From Eq 5 This is q for the system	6
$\Delta\mathbf{S}_{surr} = -5226 \text{ J} / 273 \text{ K} = -19.14 \text{ J K}^{-1}$ $\Delta\mathbf{S}$ universe $= \Delta\mathbf{S}_{gas} + \Delta\mathbf{S}_{surr} =$ 19.14 - 19.14 = 0 J K^{-1} as expected for a reversible process **Answer**	q for the surroundings is – 5226 J and T = 273	7

(b) ideal gas, 1 mol 22.4 L, 0 °C $\rightarrow$ 224 L, 0 °C irreversible expansion into evacuated vessel

Equation	Basis for the equation	Eq. #
$\Delta\mathbf{U} = 0$ $\Delta\mathbf{H} = 0$ $\Delta\mathbf{S} = 19.14 \text{ J K}^{-1}$ $\Delta\mathbf{A} = -5226$ J $\Delta\mathbf{G} = -5226$ J **Answer**	The same values hold for changes in state functions *for identical initial and final states,* regardless of the process that brought it about.	1
$\delta W = - p_{op} dV$	Definition of pV work	2
$p_{op} = 0$	Expanding into a vacuum, the gas encounters zero opposing pressure	3
$W = 0$ **Answer**	Since $p_{op} = 0$	4
$d\mathbf{U} = \delta q + \delta W$	First law of thermodynamics	5
$q = 0$ **Answer**	From Eq 4 and 5	6
$q_{surroundings} = 0$	Since no heat passed between gas and its surroundings	7
$\Delta\mathbf{S}_{surr} = 0$	Can imagine a reversible process by which the surroundings accepted zero heat from the gas at 0 °C	8
$\Delta\mathbf{S}$ universe $= \Delta\mathbf{S}_{gas} + \Delta\mathbf{S}_{surr}$ $= 19.14 \text{ J K}^{-1}$	$\Delta\mathbf{S}$ universe is positive, consistent with a spontaneous expansion of a gas into vacuum	9

3. ideal gas, 1 mol V_1, T_1 $\rightarrow$ V_2, T_2 irreversible adiabatic expansion no work done

Equation	Basis for the equation	Eq. #
$W = 0$	Given	1
$q = 0$	Given (adiabatic)	2
$d\mathbf{U} = \delta q + \delta W$	First law of thermodynamics	3
$\Delta\mathbf{U} = 0$	From Eq 1, 2 and 3	4
$d\mathbf{U} = (\partial\mathbf{U}/\partial T)_V dT + (\partial\mathbf{U}/\partial V)_T dV$	$\mathbf{U} = \mathbf{U}(T,V)$	5
$\Delta\mathbf{U} = \int C_V dT$	For an ideal gas, $(\partial\mathbf{U}/\partial V)_T = 0$	6
$dT = 0$ **Answer**	Since $\Delta\mathbf{U} = 0$ and C_V cannot be zero This is a consequence of the condition that no work is done by the gas.	7
$d\mathbf{S} = (\partial\mathbf{S}/\partial T)_V dT + (\partial\mathbf{S}/\partial V)_T dV$ $(\partial\mathbf{S}/\partial V)_T = (\partial p/\partial T)_V$ $(\partial p/\partial T)_V = R/V$ $(\partial\mathbf{S}/\partial V)_T = R/V$ $\Delta\mathbf{S} = \int (R/V)dV$	Using the same arguments as in the previous problem for 1 mole of an ideal gas undergoing a volume change and also $dT = 0$	8
$\Delta\mathbf{S} = R \ln (V_2/V_1)$	This is positive since $V_2 > V_1$ in an expansion	
$q_{surroundings} = 0$	Since no heat passed between gas and its surroundings	7
$\Delta\mathbf{S}_{surr} = 0$	Can imagine a reversible process by which the surroundings accepted zero heat from the gas at T_1	8
$\Delta\mathbf{S}$ universe $= \Delta\mathbf{S}_{gas} + \Delta\mathbf{S}_{surr}$ $= R \ln (V_2/V_1)$	$\Delta\mathbf{S}$ universe is positive, consistent with an irreversible process for the gas	9
$\Delta\mathbf{S}_{gas} = R \ln(V_2/V_1)$ since $dT=0$, ideal gas $\Delta\mathbf{U} = 0$, $q = -W$ $W = -\int RTdV/V = -RT \ln(V_2/V_1)$ $q_{gas} = RT\ln(V_2/V_1)$ $q_{surroundings} = -RT \ln(V_2/V_1)$ $\Delta\mathbf{S}_{surr} = -R \ln(V_2/V_1)$ $\Delta\mathbf{S}$ universe $= \Delta\mathbf{S}_{gas} + \Delta\mathbf{S}_{surr} = 0$ as expected for a reversible process	*If on the other hand, reversible isothermal process for 1 mol ideal gas from V_1 to V_2,* then conditions are the same as in Problem 2 and $q = -W$ where W can be calculated from $p_{op} = p_{gas}$ leading to $q_{surroundings}/T$ opposite sign to $\Delta\mathbf{S}_{gas}$	10

4. ideal gas 1 mol in contact with heat reservoir at 25°C 100 atm $\rightarrow$ 1 atm

Equation	Basis for the equation	Eq. #
$d\mathbf{S} = (\partial\mathbf{S}/\partial T)_p dT + (\partial\mathbf{S}/\partial p)_T dp$	$\mathbf{S} = \mathbf{S}(T,p)$	1
$(\partial\mathbf{S}/\partial p)_T = -(\partial V/\partial T)_p$	Derived (see lecture notes Part 4) starting from $d\boldsymbol{U} = đq_{rev} - pdV = Td\boldsymbol{S} - pdV$ and use of cross derivatives	2

$V = RT/p$ $(\partial V/\partial T)_p = R/p$ $(\partial \mathbf{S}/\partial p)_T = - R/p$	Ideal gas equation of state for one mol Differentiating Substituting Eq 4 into Eq 2	3 4 5
$\Delta \mathbf{S} = - \int (R/p)dp$	Substituting Eq 5 into Eq 1 and using dT = 0 for this problem	6
$\Delta \mathbf{S}_{gas} = -$ (1 mol)(8.314 J $mol^{-1}K^{-1}$)• ln(1/100) =+ 38.3 J $mol^{-1}K^{-1}$	In all cases, for the same initial and final conditions, regardless of whether work is done or not during the process, because **S** is a state function	7
$\Delta \mathbf{U} = 0$, $\Delta \mathbf{U} = q + W$	Ideal gas and first law of thermodynamics	8
$q_{system} = - W_{system}$	In all cases, for the same initial and final conditions, regardless of whether work is done or not during the process, because **U** is a state function and the first law of thermodynamics always holds.	
$q_{surr} = - q_{system} = W_{system}$	Any heat transferred from the system goes into the surroundings. q_{surr} is negative (the surroundings provide heat to the system) when the gas does some work	

	W_{system}	q_{surr}	$\Delta \mathbf{S}_{surr} = q_{surr}/T$	$\Delta \mathbf{S}_{gas}$	$\Delta \mathbf{S}_{universe} = \Delta \mathbf{S}_{surr} + \Delta \mathbf{S}_{gas}$
(a)	- 2730 cal = - 11422 J	- 11422 J	-11422/298 = - 38.3 J K^{-1}	+38.3 J K^{-1}	0
(b)	- 1000 cal = -4184 J	- 4184 J	-4184/298 = - 14.0 J K^{-1}	+38.3 J K^{-1}	+24.3 J K^{-1}
(c)	0 cal	0 J	0	+38.3 J K^{-1}	+38.3 J K^{-1}

5. Third law entropy of CH_3NO_2 (gas, 298.1 K, 1 atm) can be obtained by adding up the entropies for all the transformations needed for

CH_3NO_2 (perfect crystal, 0 K, 1 atm) $\rightarrow$ CH_3NO_2 (gas, 298.1 K, 1 atm)

We will use

$d\mathbf{S} = (\partial \mathbf{S}/\partial T)_p dT + (\partial \mathbf{S}/\partial p)_T dp = (C_p/T)dT - (\partial V/\partial T)_p \, dp$

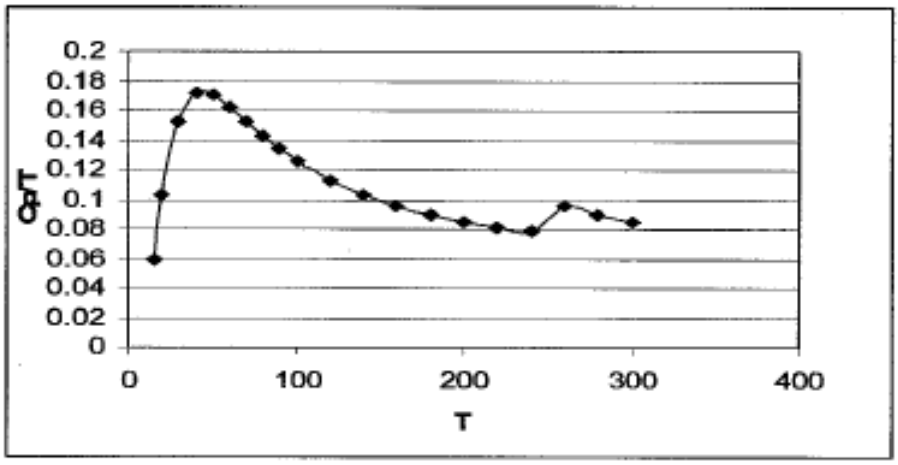
$(\partial \mathbf{S}/\partial p)_T = -(\partial V/\partial T)_p$

$d\mathbf{S} = (C_p/T)dT - (\partial V/\partial T)_p \, dp$

Since p = 1 atm, dp = 0, $d\mathbf{S} = (C_p/T)dT$; $\Delta \mathbf{S} = \int (C_p/T)dT$

For a phase transformation where dT = 0, we will use $\Delta \mathbf{S} = q_{REV,p}/T_{trans} = \Delta \mathbf{H}_{trans}/T_{trans}$

Given the table of C_p (cal mol-1 K-1) as function of T, calculate C_p/T values and plot vs T to find the integral of $(C_p/T)dT$ between 15 K and 298.1 K



CH_3NO_2 (perfect crystal, 0 K, 1 atm)	**S** = 0 at absolute 0 K for a perfect crystal (Third law of thermodynamics)	0
(crystal, 15 K, 1 atm)	for dp =0 $\Delta\mathbf{S}_1 = \int_0^{15}(C_p/T)dT$ For solids, C_p and C_v are nearly the same $C_p - C_V = -T\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial V}\right)_T$ because the two factors are small for solids, especially for low T. For perfect solids, C_V behaves asymptotically lim $_{(T \to 0\ K)}$ $C_V = aT^3$ $C_v = 464.4(T/\Theta_D)^3$ cal mol^{-1} K^{-1} $= aT^3$ where Θ_D = 215 K for Cu, for example, therefore $a = 4.67\times10^{-5}$ Debye extrapolation from 0 K to 15K Debye: $\Delta\mathbf{S}_1 = (1/3)a(15)^3 = 0.05$ cal mol^{-1} K^{-1} This seems rather small.	$\Delta\mathbf{S}_1$
(crystal, 244.7 K, 1 atm)	Integration from 15K to 244.7 K, dp =0 ($\Delta\mathbf{S}_2$) Integration over the whole range of temperatures 15K to 298.1 K gives 30.52 cal mol^{-1} K^{-1} which includes ($\Delta\mathbf{S}_2 + \Delta\mathbf{S}_4$)	$\Delta\mathbf{S}_2$
(liquid, 244.7 K, 1 atm)	Phase transition at 244.7 K $\Delta\mathbf{H} = q_{p\ REV}$ = 2319 cal mol^{-1} $\Delta\mathbf{S}_3$ = 2319 cal mol^{-1} /244.7 K = 9.48 cal mol^{-1} K^{-1}	$\Delta\mathbf{S}_3$
(liquid, 298.1, 1 atm)	Integration from 244.7 K to 298.1 K, dp = 0 ($\Delta\mathbf{S}_4$) This is already included in ($\Delta\mathbf{S}_2 + \Delta\mathbf{S}_4$) integration.	$\Delta\mathbf{S}_4$
(liquid, 298.1, 3.666 cm Hg)	Integration from 76.0 cm Hg to 3.666 cm Hg at 298.1 K for liquid, dT = 0 For the liquid, assume small temperature coefficient of volume, $(\partial V/\partial T)_p \sim 0$, leads to $(\partial\mathbf{S}/\partial p)_T = -(\partial V/\partial T)_p$	$\Delta\mathbf{S}_5$

	~ 0 $\Delta \mathbf{S}_5 = 0$	
(vapor, 298.1, 3.666 cm Hg)	Phase transition at 298.1 K, 3.666 cm Hg $\Delta \mathbf{S}_6 = 9147 \text{ cal mol}^{-1} / 298.1 \text{ K} = 30.68 \text{ cal mol}^{-1} \text{ K}^{-1}$	$\Delta \mathbf{S}_6$
(vapor, 298.1, 1 atm)	Integration from 3.666 cm Hg to 76.0 cm Hg at 298.1 K for gas, dT = 0 For the vapor, if ideal: V = RT/p $(\partial V/\partial T)_p = R/p$ $(\partial \mathbf{S}/\partial p)_T = - R/p$ $\Delta \mathbf{S}_7 = - R \ln(76.0/3.666) = - 6.03 \text{ cal mol}^{-1} \text{ K}^{-1}$	$\Delta \mathbf{S}_7$
$\mathbf{S}_{absolute} = 65.70 \text{ cal mol}^{-1} \text{ K}^{-1}$ **Answer**	$\mathbf{S}_{absolute}$ = $\mathbf{S}(0 \text{ K}) + \Delta \mathbf{S}_1 + \Delta \mathbf{S}_2 + \Delta \mathbf{S}_3 + \Delta \mathbf{S}_4 + \Delta \mathbf{S}_5 + \Delta \mathbf{S}_6 + \Delta \mathbf{S}_7$	

6. N_2 gas at 1000 atm, 1000 °C fugacity = ?

Equation	Basis for the equation	Eq. #
$\ln \frac{f}{p} = \int_0^p \frac{(Z-1)}{p} dp$	Relation of fugacity to pressure (from lecture notes Part 5)	1
$Z = pV/RT$	For a non-ideal gas, Z is not 1	2
$p(V-b) = RT$ $b = 39.1 \times 10^{-3} \text{ L mol}^{-1}$	Equation of state to be used for this gas	3
$Z = V/(V-b)$	From Eq 2 and 3	4
$Z-1 = b/(V-b)$		5
$(Z-1)/p = b/RT$	From Eq 3 and 5	6
$\int (Z-1)dp/p = (b/RT) \int_0^p dp$	From Eq 6	7
$\ln (f/p) = (b/RT)p$	From Eq 1 and 7	8
$f = p \bullet \exp(bp/RT)$	Eq 8 and definition of ln	9
$f = 1000 \text{ atm} \bullet \exp[0.0391 \text{ L mol}^{-1} \bullet 1000 \text{ atm}/(0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1} \bullet 1273 \text{ K})] = 1450 \text{ atm}$ **Answer**	Substituting values into Eq 9 and evaluating	

7. From given table of Z vs p, calculate the following:

p	1.0000	4.00000	7.00000	10.0000	40.0	70.0	100.0
(Z-1)/p	-0.00290	-0.00301	-0.00303	-0.00304	-0.00316	-0.00319	-0.00313

Equation	Basis for the equation	Eq. #
$\ln \frac{f}{p} = \int_0^p \frac{(Z-1)}{p} dp$	Relation of fugacity to pressure (from lecture notes Part 5)	1
$(Z-1)/p = -0.0031 - 2 \times 10^{-6} (p/1\text{atm})$	Fit the values in above table to a function of p. Nearly independent of p.	2

ln (f/p) = Integral ≈ - 0.31	Integral = area under this curve for p = 0 to p=100 atm has a value very close to 100•(- 0.0031)	3
f = p exp(-0.31) = 0.733p f = 73.3 atm at 100 atm, 200 K **Answer**	From Eq 3 rearrange and evaluate	

8.

Equation	Basis for the equation	Eq. #
$dG = Vdp - SdT$	One of the four fundamental equations of thermodynamics	1
$dG = (\partial G/\partial T)_p\, dT + (\partial G/\partial p)_T\, dp$	**G** = **G**(T,p)	2
$(\partial G/\partial p)_T = V$	From Eq 1 & 2	3
G = RT ln(p/1atm) + A' + B'p + (1/2)C'p^2 + (1/3)D'p^3	Given **G** = **G**(T,p) functional form	4
V = RT/p + B' + C'p + D'p^2 This is the equation of state **Answer**	Taking $(\partial G/\partial p)_T$ and equating it to V	5

9. At 100 °C and 1 atm, water and steam are at equilibrium (this point is on the liquid-vapor equilibrium curve for H_2O):

water (100 °C and 1 atm) ⇔ steam (100 °C and 1 atm)

Equation	Basis for the equation	Eq. #
H = **U** + pV	Definition	1
d**U** = δq + δW	First law of thermodynamics	2
Δ**U** = q_p - pΔV Δ**H** = Δ**U** + pΔV	At constant opposing pressure p	3
Δ**H** = q_p	At constant pressure, from 3	4
Δ**S** = q_{REV}/T	Second law of thermodynamics	5
Δ**S** = Δ**H**/T	q_{REV} is also q_p at constant pressure (1 atm) in this problem, for the phase change at 100 °C and 1 atm	6
Δ$\mathbf{S}_{vaporizn}$ = (1.76 – 0.31) cal K^{-1} g^{-1}	Given (**S**$_T$ – **S**$^{\ominus}_{298}$) = 0.31 cal K^{-1} g^{-1} for water at 100 °C and 1 atm Given (**S**$_T$ – **S**$^{\ominus}_{298}$) = 1.76 cal K^{-1} g^{-1} for steam at 100 °C and 1 atm	7
= Δ$\mathbf{H}_{vaporizn}$ / 373.1 K	From Eq 6	8
(a) Δ$\mathbf{H}_{vaporizn}$ = 373.1(1.76 – 0.31) = 541 cal g^{-1} **Answer**	Evaluating	9

(b) $\Delta \mathbf{H}_{\text{vaporizn}}$ = $\{(\mathbf{H}_T - \mathbf{H}^{\ominus}_{298})_{\text{steam}} - (\mathbf{H}_T - \mathbf{H}^{\ominus}_{298})_{\text{water}}\}$ at 100 °C and 1 atm 541 cal g^{-1} = 640 cal g^{-1} - $(\mathbf{H}_T - \mathbf{H}^{\ominus}_{298})_{\text{water}}$ $(\mathbf{H}_T - \mathbf{H}^{\ominus}_{298})_{\text{water}}$ = 99 cal g^{-1}	Using Eq 9 and given	10
(c) $\mathbf{G} = \mathbf{H} - T\mathbf{S}$	Definition	11
$\Delta\mathbf{G} = \Delta\mathbf{H} - T\Delta\mathbf{S}$	At constant T	12
$(\mathbf{G}_T - \mathbf{G}^{\ominus}_{298})_{\text{water}} = (\mathbf{H}_T - \mathbf{H}^{\ominus}_{298})_{\text{water}} - 373.1 \bullet (\mathbf{S}_T - \mathbf{S}^{\ominus}_{298})_{\text{water}}$ = 99 – 373.1•0.31 = -16.7 cal g^{-1} **Answer**	Substituting values	13
$(\mathbf{G}_T - \mathbf{G}^{\ominus}_{298})_{\text{steam}} = (\mathbf{H}_T - \mathbf{H}^{\ominus}_{298})_{\text{steam}} - 373.1 \bullet (\mathbf{S}_T - \mathbf{S}^{\ominus}_{298})_{\text{steam}}$ = 640 – 373.1•1.76 = -16.7 cal g^{-1} **Answer**	The two are equal as expected	

10. C(graphite) → C(diamond) (298 K, 1 atm)

Equation	Basis for the equation	Eq. #
$C_{(\text{diamond})} + O_2 \rightarrow CO_2$ (298 K,1 atm) $\Delta\mathbf{H}$ = 94.484 kcal mol^{-1} $C_{(\text{graphite})} + O_2 \rightarrow CO_2$ (298 K, 1 atm) $\Delta\mathbf{H}$ = 94.030 kcal mol^{-1} $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}$ (298 K, 1 atm) $\Delta\mathbf{H}$ = 94.484-94.030 = 0.454 kcal mol^{-1}	**H** is a state function	1
$\Delta\mathbf{S} = \mathbf{S}_{\text{diamond}} - \mathbf{S}_{\text{graphite}}$ = 0.5829 – 1.3609 = - 0.7780 cal K^{-1} mol^{-1}	Use given data at 298 K, 1 atm	2
$\mathbf{G} = \mathbf{H} - T\mathbf{S}$ $\Delta\mathbf{G} = \Delta\mathbf{H} - T\Delta\mathbf{S}$	Definition At constant T	3 4
$\Delta\mathbf{G}$ = 454 – 298•(- 0.7780) = 685.8 cal mol^{-1} (298 K, 1 atm) **Answer**		5
$\mathbf{G}^{\ominus}_{298}$(diamond) - $\mathbf{G}^{\ominus}_{298}$(graphite) = 685.8 cal mol^{-1}	$^{\ominus}$ means 1 atm	6
$d\boldsymbol{G} = V dp - \boldsymbol{S} dT$	One of the four fundamental equations of thermodynamics	7
$\boldsymbol{G}(T) = \boldsymbol{G}^{\ominus}_{T} + \int_1^p V\,dp$	For any pure material at a given temperature (dT=0)	8

$\mathbf{G}_{298}(\text{diamond}) = \mathbf{G}^{\ominus}_{298}(\text{diamond}) + \int_1^p V_{\text{diamond}}\, dp$ $\mathbf{G}_{298}(\text{graphite}) = \mathbf{G}^{\ominus}_{298}(\text{graphite}) + \int_1^p V_{\text{graphite}}\, dp$	Applying Eq 7 to each pure material	9
$C_{(\text{graphite})} \Leftrightarrow C_{(\text{diamond})}$ (298 K, p atm) $\mathbf{G}_{298}(\text{diamond,p}) - \mathbf{G}_{298}(\text{graphite,p}) = 0$	At equilibrium at this value of p means **G** of graphite and **G** of diamond are equal at this p and 298 K.	10
$0 = 685.8 \text{ cal mol}^{-1} + \int_1^p V_{\text{diamond}}\, dp - \int_1^p V_{\text{graphite}}\, dp$	Using Eq 6, 9 and 10	11
$0 = 685.8 \text{ cal mol}^{-1} + (1.987/0.08206)\bullet (12 \text{ g}/3.513\times10^3 \text{ g L}^{-1})(p-1) - (12 \text{ g}/2.260\times10^3 \text{ g L}^{-1})(p-1)$	Using given densities, independent of pressure and 1 mol C = 12 g and 10^3 cm^3 = 1 L and use conversion 1.98722 cal = 0.0820578 L atm	12
$0 = = 685.8 - 0.04586(p-1)$ $p-1 = 14950$ atm **Answer** for $C_{(\text{graphite})} \Leftrightarrow C_{(\text{diamond})}$ (298 K, p atm)	Solving for p	
$C_{(\text{graphite})} \Leftrightarrow C_{(\text{diamond})}$(1273 K, p atm) $\mathbf{G}_{1273}(\text{diamond,p}) - \mathbf{G}_{1273}(\text{graphite,p}) = 0$ $0 = \mathbf{G}^{\ominus}_{1273}(\text{diamond}) - \mathbf{G}^{\ominus}_{1273}(\text{graphite}) + \int_1^p V_{\text{diamond}}\, dp - \int_1^p V_{\text{graphite}}\, dp$ Solve for p	To do the same calculation for 1000°C. We need the value $\mathbf{G}^{\ominus}_{1273}(\text{diamond}) - \mathbf{G}^{\ominus}_{1273}(\text{graphite})$, for which we need molar entropies **S** at 1000°C, 1 atm, and also $\Delta\mathbf{H}$ at 1000°C, 1 atm. $\mathbf{S}_{1273}$ for graphite = 1.3609 cal K^{-1} mol^{-1} + $\int_{298}^{1273}(C_{p,\text{graphite}}/T)dT$ $\mathbf{S}_{1273}$ for diamond = 0.5829 cal K^{-1} mol^{-1} + $\int_{298}^{1273}(C_{p,\text{diamond}}/T)dT$ $\Delta\mathbf{H}_{1273}$ (graphite) = $\Delta\mathbf{H}_{298} + \int_{298}^{1273} C_{p,\text{graphite}}\, dT$ $\Delta\mathbf{H}_{1273}$ (diamond) = $\Delta\mathbf{H}_{298} + \int_{298}^{1273} C_{p,\text{diamond}}\, dT$ To estimate these quantities, we need to find C_p data for the two forms over the range 298 to 1273K.	