Name _____

Please put answers within boxes provided.

Chemistry 342

October 23, 1998

Second Exam

Answers

$1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$ $k_B = 1.38066\times10^{-23}\ \text{J K}^{-1}$ $R = N_{Avogadro}k_B$

$R = 8.31441\ \text{J mol}^{-1}\ \text{K}^{-1} = 1.98718\ \text{cal mol}^{-1}\ \text{K}^{-1} = 0.082057\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$C_p - C_V = \{ p + (\partial U/\partial V)_T \}(\partial V/\partial T)_p$

$(1/T)\{-V + (\partial H/\partial p)_T\} = -(\partial V/\partial T)_p$ $(1/T)\{ p + (\partial U/\partial V)_T\} = (\partial p/\partial T)_V$

$\mu_{JT} = (\partial T/\partial p)_H$ $(\partial H/\partial p)_T = -C_p\,\mu_{JT}$

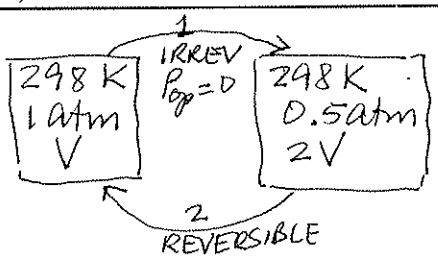
monatomic gas molar heat capacity: $C_V = (3/2)R$

1. Consider the following cycle using 1 mole of an ideal gas, initially at 25°C and 1 atm pressure.

Step (1) Isothermal expansion against zero pressure to double the volume (Joule expansion).

Step (2) Isothermal, reversible compression from 1/2 atm to 1 atm.

(a) Calculate the value of $\oint \delta q/T$.



$W = -\int P_{op}\,dV$

$n = 1$ mol

For ideal gas $U = U(T)$ so that when T does not change $\Delta U = 0$. This holds for step 1 and step 2.

Step 1. $\Delta U = q + W$ First Law

$0 = q_{IRREV} + 0$ $W = 0$ since $P_{op} = 0$

Step 2. $\Delta U = q + W$

$0 = q_{REV} - \int p\,dV$ $P_{op} = P_{gas}$ since reversible

or $dq_{REV} = +p\,dV = \dfrac{RT\,dV}{V}$ ideal gas

cycle: step 1, step 2

$$\oint \frac{dq}{T} = \int \frac{dq_{IRREV}}{T} + \int \frac{dq_{REV}}{T} = 0 + \int_{2V}^{V} \frac{RT\,dV}{T\,V} = R\ln\frac{1}{2}$$

$$= 8.3144\ \text{J mol}^{-1}\text{K}^{-1} \times 1\ \text{mol} \times \ln\tfrac{1}{2} = -5.763\ \text{J K}^{-1}$$

(b) Calculate ΔS for Step (2)

$\Delta S_2 = \int \frac{dq_{REV}}{T}$ = as shown in part (a) $= R \ln \frac{1}{2}$

$= -5.763 \, J K^{-1}$

(c) Calculate ΔS for Step (1)

$\Delta S_1 = \int \frac{dq_{REV}}{T}$

but since $\Delta S_{cycle} = 0$, $0 = \Delta S_1 + \Delta S_2$

$0 = \Delta S_1 - 5.763 \, J K^{-1}$

$\therefore \Delta S_1 = +5.763 \, J K^{-1}$

2. Given the following data for benzene, C_6H_6:

At the normal boiling point, 80.1°C , $\Delta_{vap}\boldsymbol{H}$ is 7.353 kcal mol^{-1} , and

C_p for the liquid is 31 cal mol^{-1} K^{-1}

C_p for the vapor is $-0.409 + 77.621\times10^{-3}\ T - 264.29\times10^{-7}\ T^2$ cal mol^{-1} K^{-1}

Assume that benzene vapor behaves ideally. Calculate $\Delta\boldsymbol{S}$ for the process:

C_6H_6 (liq, 82.1°C, 1 atm) → C_6H_6 (g, 82.1°C, 0.5 atm)

This is not a reversible change since gas and liquid benzene are not at equilibrium at 82.1°C as given. Therefore, we need to find ΔS by difference. Construct a cycle:

LIQ, 353.3K, 1atm ← b ~~GAS~~ 353.3K, 1atm

↓ c ↑ a

LIQ, 355.3K, 1atm → d GAS 355.3K, 0.5atm

$\Delta S_{cycle} = 0 = \Delta S_a + \Delta S_b + \Delta S_c + \Delta S_d$. Solve for ΔS_d

$$\int dS = \int \frac{C_p dT}{T} + \int \left(\frac{\partial S}{\partial p}\right)_T dp = \int \frac{C_p dT}{T} - \int \left(\frac{\partial V}{\partial T}\right)_p dp$$

(problem 3(a) derivation)

$pV = RT$ ideal GAS

$V = RT/p$

$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p dT}{T} - \int_{p_i}^{p_f} R\frac{dp}{p}$$

$$\Delta S_a = \int_{355.3}^{353.3} \frac{(-0.409 + 77.62\times10^{-3}T - 264.29\times10^{-7}T^2)}{T} dT - \int_{p_i=0.5}^{p_f=1\,atm} R\frac{dp}{p}$$

$$= -0.409 \ln\frac{353}{355} + 77.62\times10^{-3}(353-355) - 264.29\times10^{-7}\left(\frac{1}{2}\right)\left[353^2 - 355^2\right] - R\ln\left(\frac{1}{0.5}\right)$$

use 1.987 cal K^{-1} mol^{-1}

continue **2.** here $dS = dq_{rev}/T$

$$\Delta S_b = \frac{q_{rev}}{T} = \frac{-\Delta H_{vap}}{T_b} = \frac{-7.353 \times 10^3}{353.3} \text{ cal mol}^{-1} \text{K}^{-1}$$

$$\Delta S_c = \int_{353}^{355} 31 \frac{dT}{T} + 0 = 31 \ln \frac{355}{353} \text{ cal mol}^{-1} \text{K}^{-1}$$

$$0 = (31.409) \ln \frac{355}{353} + 77.62 \times 10^{-3}(-2) - 264.29 \times 10^{-7} \frac{(-1417.2)}{2} - 1.987 \ln 2$$

$$\frac{-7.353 \times 10^3}{353.3} + \Delta S_d = 0.1773 - 0.1552 + .01873 - 1.3773 + \Delta S_d$$

$$-20.812$$

$$0 = -22.15 + \Delta S_d$$

$$\therefore \Delta S_d = +22.15 \text{ cal mol}^{-1} \text{K}^{-1}$$

Or else

$$\text{LIQ, } 355.3\text{K, 1atm} \xrightarrow{(1)} \text{LIQ, } 353.3\text{K, 1atm} \xrightarrow{(2)} \text{GAS, } 353.3\text{K/1atm}$$

$$\downarrow (3)$$

$$\text{GAS, } 355.3\text{K, } 0.5\text{atm}$$

$$\Delta S_1 = \int_{355}^{353} \frac{C_p^{LIQ} dT}{T} = 31.409 \ln \frac{353.3}{355.3} = -0.1773 \text{ cal mol}^{-1} \text{K}^{-1}$$

$$\Delta S_2 = \frac{q_{rev}}{T} = \frac{\Delta_{vap}H}{T_b} = \frac{7.353 \times 10^3}{353.3} = +20.812 \text{ cal mol}^{-1} \text{K}^{-1}$$

$$\Delta S_3 = \int_{353}^{355} \frac{C_p^{GAS} dT}{T} - \int_{1atm}^{0.5atm} \frac{R dp}{p} = +0.13647 + 1.3773 = +1.5138$$

$$\text{cal mol}^{-1} \text{K}^{-1}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -0.1773 + 20.812 + 1.5138 = +22.15$$

$$\text{Cal mol}^{-1} \text{K}^{-1}$$

3. (a) Derive $(\partial S/\partial p)_T$ for an ideal gas by making use of the First and Second Law and the fact that **dG** is an exact differential.

$G \equiv H - TS \quad H = U + pV$

$dG = dU + pdV + Vdp - TdS - SdT$

First Law: $dU = dq + dW$ whether reversible or irreversible

Consider a reversible change: $dU = dq_{REV} + dW_{REV}$

Definition: $dS = dq_{REV}/T$, $dW_{REV} = -pdV$ $\rightarrow$ $dU = TdS - pdV$

Substitute into dG to get

$dG = TdS - pdV + pdV + Vdp - TdS - SdT = Vdp - SdT$

Since dG is an exact differential, therefore the cross derivatives are equal,

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

IDEAL GAS 1 mol: $PV = RT \quad V = RT/p$

$\left(\frac{\partial V}{\partial T}\right)_p = R/p$

$\therefore \left(\frac{\partial S}{\partial p}\right)_T = -R/p$ for an ideal gas

(b) One mole of liquid water (density = 1 g/mL) is allowed to expand into an evacuated flask of volume such that the final pressure is 0.3 atm. The bulb containing the liquid and the flask are thermostated so that a constant temperature of 100 °C is maintained. It is found that 11,000 cal of heat are absorbed when this process occurs. Calculate the values for ΔU, ΔH, ΔS, and ΔG. Assume vapor is ideal.

ΔU

LIQ, 1 atm, 373.2 K $\longrightarrow$ GAS, 0.3 atm, 373.2 K

$P_{op} = 0 \quad \therefore W = 0 \quad q = 11000$ cal (given)

$\Delta U = q + W = 11000$ cal $+0$

ΔH $H \equiv U + pV$

$\Delta H = \Delta U + \Delta(pV) = 11000\ \text{cal} + (pV)_{GAS}^{1\ \text{mole}} - (pV)_{LIQUID}$

neglect $(pV)_{LIQUID}$ gas assumed ideal: $pV = RT$

$\Delta H = 11000\ \text{cal} + 1.987(373) = \underline{11740\ \text{cal}}$

ΔS is not $11000/373$

Construct a cycle

LIQ, 1atm 373.2K $\xrightarrow{c}$ GAS 0.3atm 373.2K

$\downarrow a$

GAS, 1atm, 373.2K $\xleftarrow{b}$ GAS 0.3atm 373.2K

$\Delta S_{cycle} = 0 = \Delta S_a + \Delta S_b + \Delta S_c$

ΔS_a = as derived in problem 2

$= \int C_p \frac{dT}{T} - \int \left(\frac{\partial V}{\partial T}\right)_p dp = 0 - \int_{p_i}^{p_f} R \frac{dp}{p} = -1.987 \ln\left(\frac{1}{0.3}\right)$

$\Delta S_b = \frac{q_{REV}}{373.2}$ get q_{REV} for LIQ, 1atm, 373.2K $\longrightarrow$ GAS, 0.3atm 373.2K

from $\Delta U^{*} = 11000\ \text{cal} + 0$ (since $\left(\partial U/\partial V\right)_T = 0$) $\rightarrow$ GAS, 1atm 373.2K

and $W_{REV}^{*} = 1\text{atm}(V_{GAS} - V_{LIQ}) \approx R(373.2)$ (neglect) $= 740\ \text{cal}$

$\Delta S_b = -\frac{11740\ \text{cal}}{373.2\ \text{K}}$

$0 = -1.987 \ln\frac{1}{0.3} - \frac{11740}{373} + \Delta S_c \quad \therefore \Delta S_c = 33.87\ \text{cal K}^{-1}\ \text{mol}^{-1}$

ΔS continue here

ΔG As derived in 3(a): $dG = Vdp - SdT$

$\Delta G_{cycle} = 0 = \Delta G_a + \Delta G_b + \Delta G_c$ $\quad dT = 0$ for all steps

$$\Delta G_a = \int_{0.3\,atm}^{1.0} V dp = RT \int_{0.3}^{1.0} \frac{dp}{p} = RT \ln \frac{1}{0.3} = 1.987(373.2) \ln \frac{1}{0.3}$$

$$= 892.8 \text{ cal mol}^{-1}$$

$\Delta G_b = 0$ at 373.2 K Liq and Gas are at equilibrium

$$0 = 1.987(373.2) \ln \frac{1}{0.3} + 0 + \Delta G_c$$

$$\Delta G_c = -892.8 \text{ cal}$$

[Get same answer by $\Delta G = \Delta H - T\Delta S$ from

$\Delta H = 11\,740$ cal mol^{-1}

$\Delta S = 33.85$ cal K^{-1} mol^{-1}

See pages 7a and 7b for a useful overview based on this problem

An example of multiple approaches to a given problem:

Exam Problem 3(b) One mole of liquid water (density = 1 g/mL) is allowed to expand into an evacuated flask of volume such that the final pressure is 0.3 atm. The bulb containing the liquid and the flask are thermostated so that a constant temperature of 100 °C is maintained. It is found that 11,000 cal of heat are absorbed when this process occurs. Calculate the values for ΔU, ΔH, ΔS, and ΔG. Assume vapor is ideal.

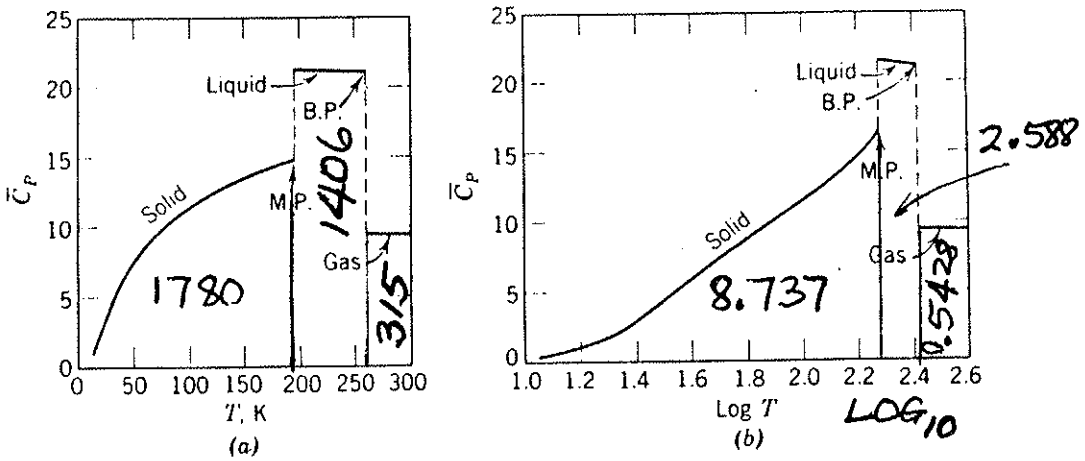
$dT = 0$ for this system

	cal mol^{-1}	from definition of the function	from relations derived from First and Second Law
ΔU	11,000	$q_{IRREV}+W_{IRREV}$ =11,000 + 0 $q_{REV}+W_{REV}$ = 12,633 + - 1633 = 11,000	$T\Delta S$ - $\int pdV$ = 12,633 - 1633 = 11,000
$\Delta(pV)$	740	$p_fV_f - p_iV_i$ = RT - 1atm×0.018 L mol^{-1} = 741.2 - 0.436 ≈ 740	
ΔH	11,740	$\Delta U + \Delta(pV)$ = 11,000 + 740 = 11,740	$T\Delta S + \int Vdp$ = 12,633 - 843 = 11,740
$T\Delta S$	12,633	q_{REV} = 12,633	
ΔG	-893	$\Delta H - T\Delta S$= 11,740 - (12,633) = -893	$-\int SdT + \int Vdp$ = 0 + (-893) = -893
$\int Vdp$	-893		
$\int pdV$	1633	$-W_{REV}$	
ΔA		$\Delta U - T\Delta S$ = 11,000 - (12,633) = -1633	$-\int pdV - \int SdT$ = -1633 + 0 = -1633
ΔS_{sys}	33.87 cal mol^{-1} K^{-1}	q_{REV}/T = 12,633/373 = 33.87 = $\Delta_{vap}H/T - \int Rdp/p$ = 11740/373 - Rln(0.3/1) = 31.47+2.39 = 33.86	
ΔS_{surr}	-29.49	$(q_{REV})_{surr}/T$ = -11,000/373 = -29.49	

	cal mol^{-1}	from considering a function of two variables
$\Delta \boldsymbol{U}$	11,000	$\Delta_{vap}\boldsymbol{U}$ = 11,000 for phase change + from $d\boldsymbol{U} = (\partial \boldsymbol{U}/\partial T)_V dT + (\partial \boldsymbol{U}/\partial V)_T dV$ = 0 + 0 total = 11,000
$\Delta(pV)$	740	
$\Delta \boldsymbol{H}$	11,740	$\Delta_{vap}\boldsymbol{H}$ = 11,740 for phase change + from $d\boldsymbol{H} = (\partial \boldsymbol{H}/\partial T)_p dT + (\partial \boldsymbol{H}/\partial p)_T dp$ = 0 + 0
$T\Delta \boldsymbol{S}$	12,633	
$\Delta \boldsymbol{G}$	-893	$\Delta_{vap}\boldsymbol{G}$ = 0 for phase change + from $d\boldsymbol{G} = (\partial \boldsymbol{G}/\partial T)_p dT + (\partial \boldsymbol{G}/\partial p)_T dp$ = $-\boldsymbol{S}dT + Vdp$ = 0 + (-893) = -893
$\int Vdp$	-893	
$\int pdV$	1633	$-W_{REV}$ *{Note that $\Delta \boldsymbol{A}$ gives the maximum work done by the system}*
$\Delta \boldsymbol{A}$		$d\boldsymbol{A} = (\partial \boldsymbol{A}/\partial T)_V dT + (\partial \boldsymbol{A}/\partial V)_T dV$ = $-\int \boldsymbol{S}dT - \int pdV$ = 0 - 1633 = -1633
$\Delta \boldsymbol{S}_{sys}$	33.87 cal mol^{-1} K^{-1}	$\Delta_{vap}\boldsymbol{H}/T$ = 11740/373 + for the next *rev* step: $d\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_p dT + (\partial \boldsymbol{S}/\partial p)_T dp$ = $0 - (\partial \boldsymbol{V}/\partial T)_p dp$ = 0 - Rln(0.3/1) = +2.39 total = 31.47+2.39 = 33.86
$\Delta \boldsymbol{S}_{surr}$	-29.49	

4. The heat capacity of sulfur dioxide at a constant pressure of 1 atm at different temperatures is shown below. At 15 K the heat capacity at constant pressure of $SO_2(s)$ is 0.90 cal mol^{-1} K^{-1}. Solid SO_2 melts at 197.64 K, $\Delta_{fus}H$ is 1769 cal mol^{-1}. At this pressure, liquid SO_2 vaporizes at 263.08 K and the $\Delta_{vap}H$ is 5960 cal mol^{-1}. The heat capacity of SO_2 gas between 300 K and 1500 K is $\{6.15 + 13.8\times10^{-3}\ T - 91.0\times10^{-7}\ T^2 + 2.06\times10^{-9}\ T^3\}$ cal $mol^{-1}K^{-1}$. Calculate the molar entropy value for SO_2 gas at 298.1 K.

Areas underneath the curves from 15 K to 298.1 K are given.



Heat capacity in cal K^{-1} mol^{-1} of sulfur dioxide at a constant pressure of 1 atm at different temperatures.

For 1 mole of SO_2 at 1 atm

$$S_{298.1} = S_{0K} + \Delta S_{(0\to15K)} + \Delta S_{(15K\to197.64K)} + \Delta S^{fus}_{197.64K} + \Delta S_{(197.64\to263.08K)} + \Delta S^{vap}_{263.08} + \Delta S_{263.08\to298.1K}$$

$S_{0K} = 0$ Third Law

$$\Delta S_{(0\to15K)} = \int_0^{15} \frac{aT^3\,dT}{T} = \int_0^{15} aT^2\,dT = \frac{aT^3}{3}\Big|_0^{15} = \frac{a}{3}(15)^3$$

Let $C_p = aT^3$ (Debye T-cubed Law)

But C_p (at 15 K) = 0.90 = $aT^3 = a(15)^3$ given

$\therefore \Delta S_{(0\to15)} = 0.30$ cal K^{-1} mol^{-1}

$$\Delta S_{(15\to197.64)} = \int_{15}^{197.64} \frac{C_p\,dT}{T} = \int_{15}^{197.64} C_p\,d(\ln T) = 2.303 \int_{15}^{197.64} C_p\,d(\log_{10} T)$$

Area under the C_p curve in C_p vs $\log_{10} T$

$= 2.303 \times 8.737$ cal K^{-1} mol^{-1}

$= 20.12$ cal K^{-1} mol^{-1}

4. continue here

$$\Delta S^{fus}_{197.64} = \frac{\Delta H^{fus}}{197.64} = \frac{1769}{197.64} = 8.95 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{(197 \rightarrow 263.08)} = 2.303 \times \underbrace{2.588}_{\text{area under the } C_p \text{ curve}} = 5.96 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\Delta S^{vap}_{263.08K} = \frac{\Delta H^{vap}}{263.08} = \frac{5960}{263.08} = 22.65 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{(263.08 \rightarrow 298.1K)} = 2.303 \times \underbrace{0.5428}_{\text{area under the } C_p \text{ curve}} = 1.25 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$S_{298.1K} = 0.30 + 20.12 + 8.95 + 5.96 + 22.06 + 1.25$$
$$= 59.64 \text{ cal K}^{-1} \text{ mol}^{-1}$$

5. Two moles of a gas whose equation of state is $pV = RT + ap$ where $a = 0.020$ L mol^{-1} at 300 K, 0.025 L mol^{-1} at 400 K, 0.030 L mol^{-1} at 500 K, undergoes isothermal compression at 300 K from 1 atm to 11 atm. Calculate ΔU, ΔG, ΔS, ΔA, and ΔH for the gas. First, derive the expressions that are appropriate for this ***non-ideal*** equation of state.

In this space, derive the expressions that are appropriate for this ***non-ideal*** equation of state, that you will need in the calculations of the changes in thermodynamic quantities.

Not an ideal gas, therefore we will start with the 2 equations (GENERAL) given on page 1 to derive $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial H}{\partial p}\right)_T$:

$\frac{1}{T}\left\{-V + \left(\frac{\partial H}{\partial p}\right)_T\right\} = -\left(\frac{\partial V}{\partial T}\right)_p$ given

or $\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$

Given $pV = RT + ap$ where $a = a(T)$

rearr. $V = \frac{RT}{p} + a$

$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \frac{da}{dT}$

$\rightarrow V - T\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{RT}{p} + a\right) - T\left(\frac{R}{p} + \frac{da}{dT}\right)$

$= a - T\frac{da}{dT}$

$\therefore \left(\frac{\partial H}{\partial p}\right)_T = a - T\frac{da}{dT}$ *

$\frac{1}{T}\left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} = \left(\frac{\partial p}{\partial T}\right)_V$ given

or $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT^2 da/dT}{(V-a)^2}$ *

Start with $p = \frac{RT}{V-a}$

$\left(\frac{\partial p}{\partial T}\right)_V = R\left\{\frac{1}{V-a} + \frac{T\frac{da}{dT}}{(V-a)^2}\right\}$

$= \frac{R}{V-a} + \frac{RT\,da/dT}{(V-a)^2}$

$T\left(\frac{\partial p}{\partial T}\right)_V - p = T\left(\frac{R}{V-a} + \frac{RT\,da/dT}{(V-a)^2}\right) - \frac{RT}{V-a}$

$T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{RT^2}{(V-a)^2}\frac{da}{dT}$

As already derived in prob. 3a)

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

$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \frac{da}{dT}$ done above

$\therefore \left(\frac{\partial S}{\partial p}\right)_T = -\left[\frac{R}{p} + \frac{da}{dT}\right]$ *

continue here derivations, as needed

a changes linearly with T 0.005 in 100 K

$\therefore a = 0.02 + 0.005 \times 10^{-2} (T - 300)$ L mol^{-1}

$\frac{da}{dT} = 0.005 \times 10^{-2}$ L mol^{-1} K^{-1}

ΔU $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$. This problem has $dT = 0$

$$\therefore \Delta U = \int \left(\frac{\partial U}{\partial V}\right)_T dV = RT^2 \frac{da}{dT} \int_{V_i}^{V_f} \frac{dV}{(V-a)^2} = RT^2 \frac{da}{dT} \left[\frac{-1}{V-a}\right]_{V_i}^{V_f}$$

$$= RT^2 \frac{da}{dT} \left[\frac{1}{V_i - a} - \frac{1}{V_f - a}\right] = T \frac{da}{dT} [P_i - P_f]$$

$$= (300\text{K})(0.005 \times 10^{-2} \text{ L mol}^{-1} \text{K}^{-1})(1 - 11)\text{atm} = -0.15 \text{ L atm mol}^{-1}$$

$\Delta U = -0.30$ L atm for 2 moles

can convert this to J by $\times \frac{8.3144 \text{ J}}{0.082056 \text{ L atm}}$ to get -30.4 J

$\Delta U = \underline{-30.4 \text{ J}}$

ΔG as derived in Prob. 3a) $dG = Vdp - SdT$. Here $dT = 0$

$$\therefore \Delta G = \int_{p_i}^{p_f} V\,dp = \int_1^{11\,atm} \left(\frac{RT}{p} + a\right) dp = RT \ln \frac{11}{1} + a(11-1)$$

(a = .02 at 300 K)

$$= .082057 \frac{L\,atm}{mol\,K} \times 300\,K \times \ln \frac{11}{1} + 0.20\ L\,mol^{-1}\,atm = 59.23\ L\,atm\,mol^{-1}$$

For 2 moles

$\Delta G = 118.46\ L\,atm$ or $\underline{12\ kJ}$

. . . . . .

or else $\Delta G = \Delta H - T\Delta S$ since T constant = same answer

(ΔH, ΔS: get these from below)

$$= 10.133\ J - 300(-39.975)\ J = 12\ kJ$$

ΔS $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$ Here $dT = 0$

$p_f = 11\,atm$

$$\therefore \Delta S = \int \left(\frac{\partial S}{\partial p}\right)_T dp = -\int_{p_i = 1\,atm} \left(\frac{R}{p} + \frac{da}{dT}\right) dp = -R \ln \frac{p_f}{p_i} - \frac{da}{dT}(p_f - p_i)$$

$$= -0.082056 \frac{L\,atm}{mol\,K} \ln \frac{11}{1} - (.005 \times 10^{-2} \frac{L}{mol\,K})(11-1)\,atm$$

$$= -.1967_6 - 5 \times 10^{-4} = -0.19726\ L\,atm\,mol^{-1}K^{-1}$$

For 2 moles

$\Delta S = -0.3945\ L\,atm\,K^{-1}$ or $\underline{-39.975\ J\,K^{-1}}$

ΔA $A \equiv U - TS \quad dT = 0 \quad \therefore \Delta A = \Delta U - T\Delta S$

ΔU set from above

$\Delta A = -30.4\ J - 300\ K(-39.975\ J\ K^{-1}) = +11962.1\ J$

---

or else,

$dA = -pdV - SdT \quad dT = 0$

$\therefore \Delta A = -\int p dV = -\int_{V_i}^{V_f} \frac{RT}{V-a} dV = -RT \ln \frac{V_f - a}{V_i - a} = -RT \ln \frac{P_i}{P_f}$

$= -8.3144(300) \ln \frac{1}{11} = +5981.1\ J$

for 2 moles $\Delta A = +11962.2\ J$

ΔH $dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$. Since $dT = 0$ here,

$\Delta H = \int \left(\frac{\partial H}{\partial p}\right)_T dp$ (derived earlier)

$\Delta H = \left(a - T\frac{da}{dT}\right)\int_{P_i}^{P_f} dp$

$= \left[0.020\ \text{L mol}^{-1} - 300\ \text{K}\left(0.005 \times 10^{-2}\ \text{L mol}^{-1}\text{K}^{-1}\right)\right](P_f - P_i) = 0.05\ \text{L atm mol}^{-1}$

$(P_f - P_i) = 11 - 1$

For 2 moles

$\Delta H = 0.10$ Latm or $10.133\ J$

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or $\Delta H = \Delta U + \Delta(pV) \quad \Delta(pV) = \Delta(RT + ap) = a(P_f - P_i) = 0.20\ \frac{\text{L atm}}{\text{mol}}$

ΔU from previous calc.

$\Delta(pV)$ for 2 moles $= 0.40$ Latm

$= -0.30\ \text{Latm} + 0.40 = +0.10$ Latm or $10.133\ J$