Print in upper case the first three letters of your last name here: ☐☐☐

Your name: Jameson

Chemistry 342

Second Exam

October 22, 1999

1 J = 1 kg m^2 s^{-2} $k_B = 1.38066\times10^{-23}$ J K^{-1} $R = N_{Avogadro}k_B$ 1.01325 bar = 1 atm

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

$p/p_0 = \exp[-(M/RT)gz]$ *barometric formula where* g = 9.80665 m s^{-2}

van der Waals equation : $(p + a/V_m^2)(V_m - b) = RT$

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

General relations for any equation of state:

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

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

1. For each of the following processes, **state which of the quantities** ΔU, ΔH, ΔS, ΔA, ΔG, q, W **are equal to zero** for the system specified.

(a) A non-ideal gas is taken around a Carnot cycle.

(b) A non-ideal gas is adiabatically expanded through a throttling valve (as in the Joule-Thomson experiment).

(c) An ideal gas is adiabatically expanded through a throttling valve, as above.

(d) Liquid water is vaporized at 100°C and 1 atm.

(e) H_2 and O_2 react to form H_2O in a thermally isolated bomb.

(f) HCl and NaOH react to form H_2O and NaCl in an aqueous solution at constant T and p.

Enter the zeros into the table and provide a brief explanation

	ΔU	ΔH	ΔS	ΔA	ΔG	q	W	Explain
(a)	0	0	0	0	0			for any cycle for any substance for any state function
* (b)		0				0		adiabatic and isenthalpic
* (c)		0				0		adiabatic and isenthalpic
(d)					0			at equilibrium at this T and p
(e)	0					0	0	adiabatic, and $dV = 0$
(f)							0	no gases and no other work

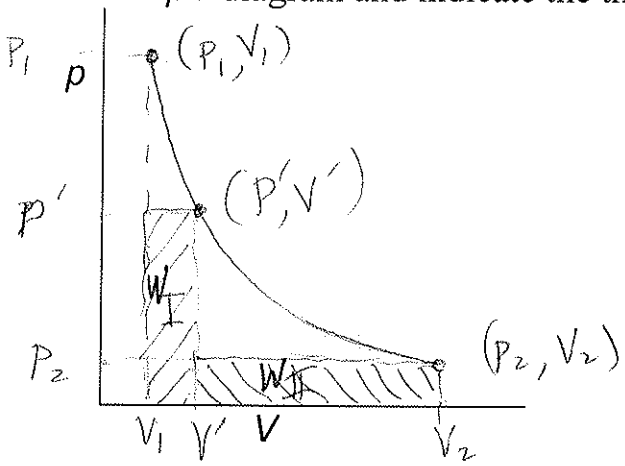
* if non-ideal, observe $(\partial T/\partial p)_H \neq 0$

if ideal, observe $(\partial T/\partial p)_H = 0$

2. One mole of an ideal gas is expanded from (T, p_1, V_1) to (T, p_2, V_2) in two stages:

	opposing pressure	volume change
First stage I	P' (constant)	V_1 to V'
Second stage II	p_2 (constant)	V' to V_2

We specify that the point (P', V') lies on the isotherm at the temperature T.
Draw the pV diagram and indicate the three points on the isotherm and the work.



(a) **Formulate the expression for the work** produced in this expansion in terms of T, p_1, p_2, and P' only. Derive the relations below and place the final expressions into the table.

$dW = -P_{op}\,dV$

$W_I = -P'\int_{V_1}^{V'} dV = -P'(V'-V_1)$ $\qquad W_{II} = -P_2\int_{V'}^{V_2} dV = -P_2(V_2-V')$

ideal gas $pV = RT$ $\qquad V_1 = \frac{RT}{P_1}$; $V_2 = \frac{RT}{P_2}$; $V' = \frac{RT}{P'}$

$W_I = -P'\left(\frac{RT}{P'} - \frac{RT}{P_1}\right)$ $\qquad W_{II} = -P_2\left(\frac{RT}{P_2} - \frac{RT}{P'}\right)$

$= -RT\left(1 - \frac{P'}{P_1}\right)$ $\qquad W_{II} = -RT\left(1 - \frac{P_2}{P'}\right)$

$W = W_I + W_{II} = -RT\left[2 - \frac{P'}{P_1} - \frac{P_2}{P'}\right]$

	W
First stage	$W_I = -RT\left(1 - \frac{P'}{P_1}\right)$
Second stage	$W_{II} = -RT\left(1 - \frac{P_2}{P'}\right)$
Overall	$W = -RT\left[2 - \frac{P'}{P_1} - \frac{P_2}{P'}\right]$

(b) **For what value** of P′ does the work produced in this 2-stage expansion have a maximum value and **what is the maximum value of the work** produced under that condition?

The mathematical condition for an extremum is that deriv = 0

To find maximum W, set $\frac{dW}{dP'} = 0$ and solve for P'

$W = -RT\left[2 - \frac{P'}{P_1} - \frac{P_2}{P'}\right)$ $\quad \frac{dW}{dP'} = -RT\left[0 - \frac{1}{P_1} + \frac{P_2}{(P')^2}\right] = 0$

$-\frac{1}{P_1} + \frac{P_2}{(P')^2} = 0 \quad \frac{1}{P_1} = \frac{P_2}{(P')^2}$ or $P' = \pm\sqrt{P_1 P_2}$ choose positive root

For this value, $P' = \sqrt{P_1 P_2}$,

$$W = -RT\left[2 - \frac{\sqrt{P_1 P_2}}{P_1} - \frac{P_2}{\sqrt{P_1 P_2}}\right] = -RT\left[2 - \sqrt{\frac{P_2}{P_1}} - \sqrt{\frac{P_2}{P_1}}\right]$$

$$W = -2RT\left[1 - \sqrt{\frac{P_2}{P_1}}\right]$$

3. (a) **Derive** the value of $(\partial S/\partial V)_T$ for the van der Waals gas, starting from the first and second law, and the properties of an exact differential such as **dA**.

First law $dU = dq + dW$, for reversible change $dU = dq_{REV} + dW_{REV}$

Second law $dS = \frac{dq_{REV}}{T}$ $\quad dU = TdS - pdV$

$dW_{REV} = -pdV$ — use these

$A \equiv U - TS$; $dA = dU - TdS - SdT$

$dA = (TdS - pdV) - TdS - SdT$

$dA = -pdV - SdT$

Since dA is an exact differential, the second mixed derivatives of A are equal:

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

(b) **Derive an expression for the change in entropy** for the isothermal expansion of one mole of the van der Waals gas from V_1 to V_2.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{as derived above}$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

van der Waals gas $\left(P + a/V^2\right)(V-b) = RT$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{(da/dT)}{V^2} + \frac{R}{(V-b)^2}\left(\frac{db}{dT}\right)$$

$+ \frac{R}{(V-b)^2}\left(\frac{db}{dT}\right)$

When $dT = 0$ (isothermal)

$$dS = \left[\frac{R}{V-b} - \frac{(da/dT)}{V^2}\right] dV \quad \text{now integrate:}$$

$$\Delta S = \int dS = \int_{V_1}^{V_2} \frac{R\,dV}{V-b} - \int_{V_1}^{V_2} (da/dT)\frac{dV}{V^2} + \int_{V_1}^{V_2} \frac{R\,dV}{(V-b)^2}\left(\frac{db}{dT}\right)$$

$$\Delta S = R \ln \frac{V_2 - b}{V_1 - b} + \frac{da}{dT}\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + R\left(\frac{1}{V_2 - b} - \frac{1}{V_1 - b}\right)\left(\frac{db}{dT}\right)$$

4. Naphthalene ($C_{10}H_8$) melts at 80°C at 1 atm pressure. Its enthalpy of fusion is 19.29 kJ mol^{-1} at 80°C, and 19.20 kJ mol^{-1} at 70°C. The heat capacity of the liquid is 223.1 J K^{-1} mol^{-1}, and that of the solid is 214 J K^{-1} mol^{-1}. **Calculate the entropy change** of the naphthalene and of the surroundings when 1 mol of liquid naphthalene supercooled to 70°C freezes to solid at 70°C. Is this a spontaneous event?

need ΔS for (LIQ, 343K, 1atm) (initial) $\longrightarrow$ (SOLID, 343K, 1atm) (final)

This is not a reversible process, SOLID + LIQ not at equilibrium at 70°C at 1atm

Consider 3 steps

LIQ, 343K, 1atm $\longrightarrow$ LIQ 353K, 1atm (a)

LIQ, 353K, 1atm $\longrightarrow$ SOLID, 353K, 1atm (b)

SOLID, 353K, 1atm $\longrightarrow$ SOLID, 343K, 1atm (c)

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$\Delta S = \Delta S_a + \Delta S_b + \Delta S_c$

For the reversible heating and cooling with no change in phase

$\int dS = \int \frac{dq_{REV}}{T} = \int \frac{C_p dT}{T}$

[or else think of S as a function of T and p

$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$. Here every step has $dp = 0$]

$\Delta S_a = \int_{343}^{353} C_p^{LIQ} \frac{dT}{T} = 223.1 \ln \frac{353}{343}$

$\Delta S_b = \frac{q_{REV,P}}{T} = \frac{-\Delta H_{FUS}}{353} = \frac{-19.29 \times 10^3}{353}$

$\Delta S_c = \int_{353}^{343} C_p^{SOLID} \frac{dT}{T} = 214 \ln \frac{343}{353}$

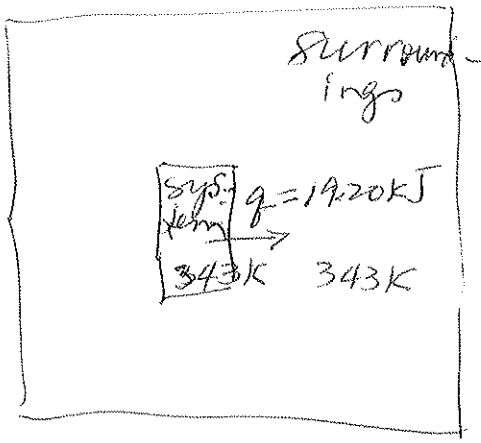
$\Delta S = 223.1 \ln \frac{353}{343} - \frac{19.29 \times 10^3}{353} + 214 \ln \frac{343}{353}$

$\Delta S = 9.1 \ln \frac{353}{343} - \frac{19.29 \times 10^3}{353} = -54.38 \text{ J K}^{-1} \text{mol}^{-1}$

$\Delta S_{surroundings} = +\frac{19.20 \times 10^3}{343} = +55.98 \text{ J K}^{-1} \text{mol}^{-1}$

$\Delta S_{universe} = +1.6 \text{ J K}^{-1} \text{mol}^{-1}$

$\Delta S > 0$ for an isolated system means event is spontaneous



1 bar = 0.987 atm

5. (a) The vapor pressure of water at 298 K is 0.0313 atm. Assume the vapor behaves ideally. **Calculate** $\Delta G^{\ominus}_{T=298K}$ in kcal mol^{-1} for the change $H_2O(g) \rightarrow H_2O(l)$.

event to be considered: (GAS, 1 bar, 298K) → (LIQ, 1 bar, 298K) not at equilibrium

Use 3 steps (GAS, 1 bar, 298K) → (GAS, 0.0313 atm, 298K) (a)

(GAS, 0.0313 atm, 298K) → (LIQ, 0.0313 atm, 298K) (b)

(LIQ, 0.0313 atm, 298K) → (LIQ, 1 bar, 298K) (c)

$\Delta G^{\ominus}_{298} = \Delta G_a + \Delta G_b + \Delta G_c$

Use $dG = Vdp - SdT$ ← $dT = 0$ here

Derive from $G \equiv H - TS$, $dG = dU + pdV + Vdp - TdS - SdT$, 1st law $dU = dq_{rev} - pdV = TdS - pdV$, $dG = Vdp - SdT$

$$\Delta G_a = \int_{0.987}^{0.0313} V_{GAS}\,dp = \int \frac{RT}{p}\,dp = R 298 \ln \frac{0.0313}{0.987}$$

$\Delta G_b = 0$ at equilibrium

$$\Delta G_c = \int_{0.0313}^{0.987} V_{LIQ}\,dp = 18\times10^{-3}(0.987 - 0.0313)\ \text{L atm mol}^{-1}$$ SMALL!

$$\Delta G^{\ominus}_{298} = \left[1.987 \times 298 \ln \frac{0.0313}{0.987} + 0 + 18\times10^{-3}(0.987 - 0.0313)\frac{1.987}{0.082057}\right] \times 10^{-3}$$

$= -2.04$ kcal mol^{-1}

(b) Suppose that the energy per mole of a van der Waals fluid has the form $U = F(T) - a/V_m$. At a given temperature, **find the difference** between the energy of water as a gas and the energy of liquid water, assuming that $V_{m,\,gas} = 24$ L mol^{-1} and $V_{m,\,liq} = 18$ cm^3 mol^{-1}. Assume that water behaves as a van der Waals fluid with $a = 5.72$ L^2 atm mol^{-2}.

$$\Delta U = U_{gas} - U_{LIQ} = \left(F(T) - \frac{a}{V_{GAS}}\right) - \left(F(T) - \frac{a}{V_{LIQ}}\right)$$

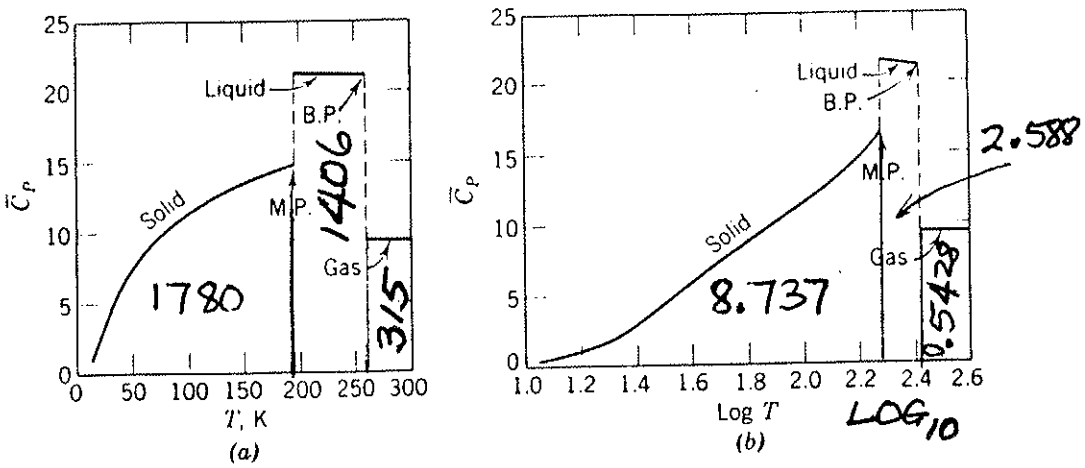
$$= +a\left(\frac{1}{V_{LIQ}} - \frac{1}{V_{GAS}}\right)$$

$$= 5.72\ \text{L}^2\text{atm mol}^{-2}\left(\frac{1}{18\times10^{-3}\ \text{L mol}^{-1}} - \frac{1}{24\ \text{L mol}^{-1}}\right)$$

$\Delta U = 317.5$ L atm mol^{-1}

or 32.17 kJ mol^{-1}

6. 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 1 atm, 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 one mol of SO_2 gas at 1 atm

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

$S_{0K} = 0$ Third Law

$$\Delta S_{(0\to15K)} = \int_0^{15} \frac{aT^3}{T} dT \quad \text{using } C_p = aT^3 \text{ Debye-Tauber Law}$$

$$= \int_0^{15} aT^2 dT = \frac{aT^3}{3}\Big|_0^{15} = \frac{a}{3}(15)^3$$

But C_p at 15K is given: $0.90\ cal\ mol^{-1}K^{-1} = aT^3 = a(15)^3$

$$\therefore \Delta S_{(0\to15K)} = \frac{0.90}{3} = 0.30$$

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

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

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

$$= 2.303 \times 8.737$$

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

$$\Delta_{fus} S_{197.64} = \frac{q_{REV,P}}{T} = \frac{\Delta_{fus} H}{197.64} = \frac{1769}{197.64} = 8.95 \text{ cal } K^{-1} \text{ mol}^{-1}$$

$$\Delta S_{(197.64 \to 263.08K)} = 2.303 \times \underbrace{2.588}_{\text{area under the curve}} = 5.96 \text{ cal } K^{-1} \text{ mol}^{-1}$$

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

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

$$S_{298.1K} = 0.30 + 20.12 + 8.95 + 5.96 + 22.65 + 1.25$$

$$= 59.23 \text{ cal } K^{-1} \text{ mol}^{-1}$$