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Chemistry 342

Second Exam

October 22, 1999

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

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

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

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:

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

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

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 in the Joule-Thomson experiment).

(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.

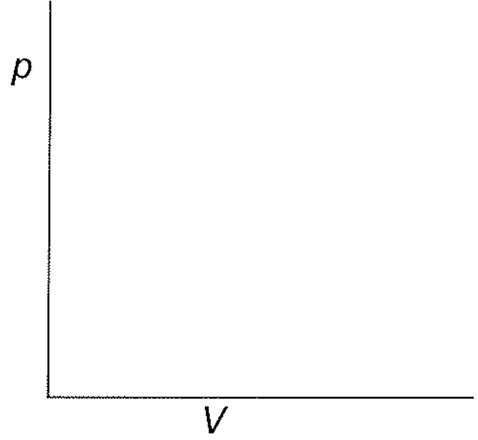
Enter the zeros into the table and provide a brief explanation

	ΔU	ΔH	ΔS	ΔA	ΔG	q	W	*Explain why zero*
(a)								
(b)								
(c)								
(d)								
(e)								
(f)								

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.

	W
First stage	
Second stage	
Overall	

(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?

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 d***A*** .

(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 .

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?

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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 $H_2O(g) \rightarrow H_2O(l)$.

(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}.

6. The heat capacity of sulfur dioxide at a constant pressure of 1 atm at different temperatures is shown below.

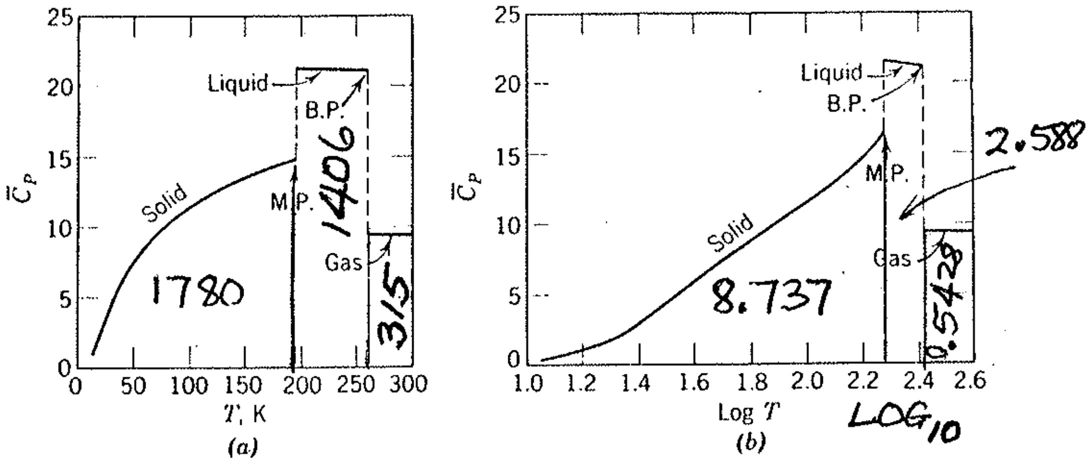
At 15 K the heat capacity at constant pressure of $SO_2(s)$ is 0.90 cal mol^{-1} K^{-1}.

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.