

2018 SPRING Semester Final Examination For General Chemistry I

Date: June 18 (Mon), **Time Limit:** 19:00 ~ 21:00

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Printed on every page.

Prof. Name	Class	Student I.D. Number	Name	
Problem	points	Problem	points	TOTAL pts
1	/6	7	/9	/100
2	/7	8	/7	
3	/9	9	/7	
4	/6	10	/9	
5	/12	11	/10	
6	/10	12	/8	

** This paper consists of 13 sheets with 12 problem sets (pages 11 & 12: constants & periodic table, page 13: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the Answer sheet.

Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.

(채점 답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure

- Return and Claim Period: **June 20 (Wed, 15: 00 ~ 17:00 p.m.)**
- Location: Room in Creative Learning Bldg. (E11)**

Class	Room	Class	Room	Class	Room
A	203	D	207	G	211
B	205	E	208		
C	206	F	210		

- Procedure:

Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)

Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

(During the period, you can check the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it. The claim is permitted only on the period. Keep that in mind! A solution file with answers will be uploaded on **June 20** on the web.)

2. Final Confirmation

- Period: June 21 (Thu)
- Procedure: During this period, you can check final score of the examination *on the website* again.

**** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr.**

1. (Total 6 pts)

(a) The air over an unknown liquid is saturated with the vapor of that liquid at 25 °C and a total pressure of 0.980 atm. Suppose that a sample of 6.00 L of the saturated air is collected and the vapor of the unknown liquid is removed from that sample by cooling and condensation. The pure air remaining occupies a volume of 3.75 L at -50 °C and 1.000 atm. Calculate the vapor pressure of the unknown liquid at 25 °C.

(Answer)

(b) Among the seven species below, choose two species whose boiling points are the closest to that of the unknown species above.

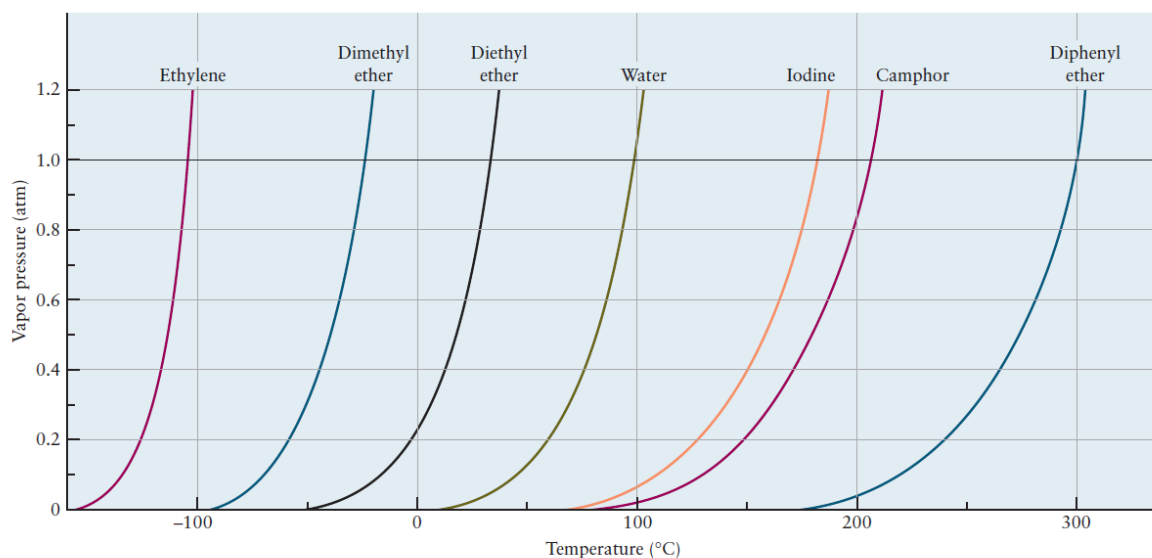


FIGURE 10.17 The vapor pressure of a solid or liquid depends strongly on temperature. The temperature at which the vapor pressure becomes 1 atm defines the normal boiling point of a liquid and the normal sublimation point of a solid.

(Answer)

2. (Total 7 pts)

(a) Arrange the following substances in order of decreasing critical temperature (T_c) :

Ar, H₂, Kr, CCl₃F

(Answer)

(b) Which of the following substances should we expect to have the lower vapor pressure at a given temperature :

(1) CO₂ or SO₂

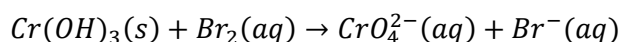
(Answer)

(2) CH₃OCH₃ or CH₃CH₂OH

(Answer)

3. (Total 9 pts)

(a) Balance the following reaction that takes place in basic solution.



(Answer)

(b) 103.0 g Cr(OH)₃ solid powder is added to the solution that contains 0.3 mol Br₂ and 2 mol NaOH dissolved in 1 kg water. Estimate the freezing point of the solution after the reaction is completed, assuming $K_f = 1.86 \text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$. (Atomic mass: H, 1.008; O, 15.999; Na, 22.990; Cr, 51.996; Br, 79.904).

(Answer)

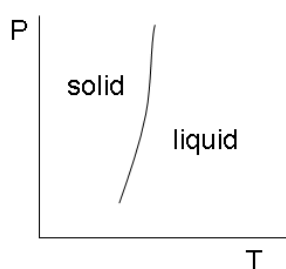
4. (Total 6 pts)

(a) At its melting point ($624\text{ }^{\circ}\text{C}$) at 1 atm, the density of solid plutonium is 16.24 g/cm^3 while the density of the liquid is 16.66 g/cm^3 . Predict what phase changes, if any, will occur when a small sample of liquid plutonium at $625\text{ }^{\circ}\text{C}$ is strongly compressed isothermally.

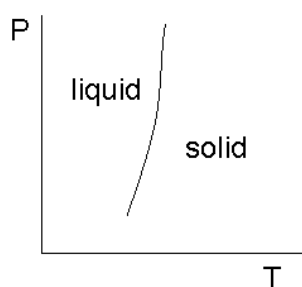
(Answer)

(b) If the phase diagram is drawn for plutonium at the liquid-solid boundary around 1 atm and $624\text{ }^{\circ}\text{C}$, what will it look like?

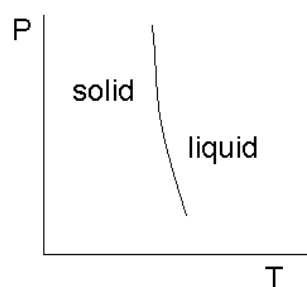
(1)



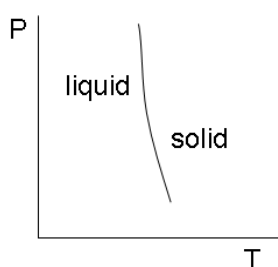
(2)



(3)



(4)



Give a reasoning for your answer as briefly as possible.

(Answer)

5. (Total 12 pts) One mole of liquid water is allowed to equilibrate with its vapor inside a one-liter vessel. The vapor pressure at 20 °C is then found to be 17.5 torr.

(a) How many moles of water exist in the vapor state? Assume ideal behavior.

(Answer)

(b) Suppose that the volume of the vessel is doubled to 2L. What is the new vapor pressure?

(Answer)

(c) How many moles of water vapor are present in the larger container?

(Answer)

(d) Water's vapor pressure falls from 17.5 torr at 20 °C to 9.2 torr at 10 °C. If equilibrium is first established at 20 °C in a volume of 1 L, then approximately how many mL of water will condense when the temperature is lowered to 10 °C? Assume that liquid water has a density of 1 g/mL.

(Answer)

(e) The vapor pressure of water/ sucrose solution ($C_{11}H_{22}O_{11}$, table sugar) is found to be 16.1 torr at 20 °C, lower by 1.4 torr compared with pure water. The solution, presumed to be ideal, contains 500 g of water. Compute the molality.

(Answer)

6. (Total 10 pts) A sample of pure solid naphthalene (C_{10}H_8) weighing 0.6410 g is burned completely with oxygen to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ in a constant-volume calorimeter at 25°C . The amount of heat evolved is observed to be 25.79 kJ. (the M_w of C_{10}H_8 is 128.17g/mol, $R = 8.3145\text{J K}^{-1} \text{mol}^{-1}$)

(a) Write and balance the chemical equation for the combustion reaction.

(Answer)

(b) Calculate the standard change in internal energy (ΔU°) for the combustion of 1.000 mol naphthalene to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$.

(Answer)

(c) Calculate the standard enthalpy change (ΔH°) for the same reaction as in part (b).

(Answer)

7. (Total 9 pts) Suppose 2.00 mol of a monatomic ideal gas is initially at a pressure of 3.00 atm and a temperature $T = 350\text{ K}$. It is expanded irreversibly and adiabatically ($q = 0$) against a constant external pressure of 1.00 atm until the volume has doubled.

(a) Calculate the final volume.

(Answer)

(b) Calculate w and ΔU for this process, in joules.

(Answer)

(c) Calculate the final temperature of the gas.

(Answer)

8. (Total 7 pts)

(a) Calculate the entropy of crystal made of 1 mol carbon monoxide (CO) at $T = 0\text{K}$ when CO molecules are in random, but parallel arrangement.

(Answer)

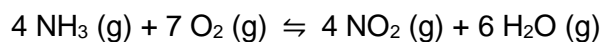
(b) Dichloromethane (CH_2Cl_2) is one of the methane (CH_4) derivatives. If 1 mol of CH_2Cl_2 adopts a random arrangement in its crystal form, what would be its entropy value at $T = 0\text{K}$?

(Answer)

9. (Total 7 pts) Calculate ΔS_{sys} , ΔS_{surr} , and ΔS_{tot} for the irreversible isothermal expansion at 298 K of 5.00 mol of an ideal gas from a pressure of 10.0 atm to constantly held external pressure of 1.00 atm.

(Answer)

10. (Total 9 pts) For the reaction equilibrium,



(a) Calculate ΔG° and the equilibrium constant K at 25°C for the reaction with the standard free energies of formations, ΔG_f° , in kJ/mol: H_2O , -228.59; NH_3 , -16.48; NO_2 , 51.29.

(Answer)

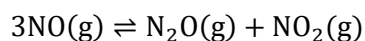
(b) Calculate ΔG° and the equilibrium constant K at 0 °C for the reaction with the standard enthalpy of formations, ΔH_f° , in kJ/mol: H_2O , -241.82; NH_3 , -46.11; NO_2 , 33.18. Assume that standard reaction enthalpy (ΔH°) and entropy (ΔS°) do not change at different temperatures.

(Answer)

(c) Calculate the standard entropy of O_2 at 25°C given with the other standard entropies at the same temperature in J/K·mol: H_2O , 188.72; NH_3 , 192.34; NO_2 , 239.95.

(Answer)

11. (Total 10 pts) Explain the effect of each of the following stresses (from right to left, from left to right, or no effect) on the position of the following equilibrium:



The reaction as written is exothermic.

(a) $\text{N}_2\text{O}(\text{g})$ is added to the equilibrium mixture without change of volume or temperature.

(Answer)

(b) The volume of the equilibrium mixture is reduced at constant temperature.

(Answer)

(c) The equilibrium mixture is cooled.

(Answer)

(d) Gaseous argon (which does not react) is added to the equilibrium mixture while both the total gas pressure and the temperature are kept constant.

(Answer)

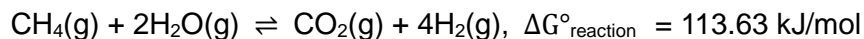
(e) Gaseous argon is added to the equilibrium mixture without changing the volume.

(Answer)

12. (Total 8 pts) Below equation is Van't Hoff equation, which explains the relationship between temperature and equilibrium constants.

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

(a) Calculate the equilibrium constant of next reaction at standard condition. Is the reaction at this condition forward favored or backward favored?



(Answer)

(b) Compute the new equilibrium constant when the reaction temperature was elevated to 1000 K. Use next value of given table. Is the new equilibrium forward favored or backward favored?

	CH ₄ (g)	H ₂ O(g)	CO ₂ (g)	H ₂ (g)
$\Delta H^\circ_{\text{formation}}$ (kJ mol ⁻¹)	-74.9	-241.8	-393.5	0

(Answer)

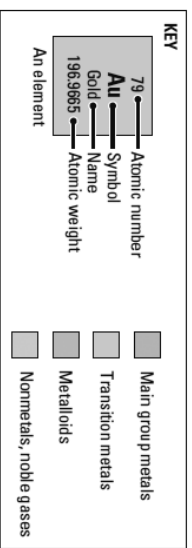
Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ \AA} = 5.2917720859 \times 10^{-11} \text{ m}$
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19} \text{ C}$
Faraday constant	$F = 96485.3399 \text{ C mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31} \text{ kg}$
Proton	$m_p = 1.672621637 \times 10^{-27} \text{ kg}$
Neutron	$m_n = 1.674927211 \times 10^{-27} \text{ kg}$
Permittivity of vacuum	$\epsilon_0 = 8.854187817 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$
Planck's constant	$h = 6.62606896 \times 10^{-34} \text{ J s}$
Ratio of proton mass to electron mass	$m_p / m_e = 1836.15267247$
Speed of light in a vacuum	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$ (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665 \text{ m s}^{-2}$ (exactly)
Universal gas constant	$R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1}$

Values are taken from the 2006 CODATA recommended values, as listed by the National Institute of Standards and Technology.

Conversion factors

Ångström	$1 \text{ \AA} = 10^{-10} \text{ m}$
Atomic mass unit	$1 \text{ u} = 1.660538782 \times 10^{-27} \text{ kg}$ $1 \text{ u} = 1.492417830 \times 10^{-10} \text{ J} = 931.494028 \text{ MeV}$ (energy equivalent form $E = mc^2$)
Calorie	$1 \text{ cal} = 4.184 \text{ J}$ (exactly)
Electron volt	$1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J} = 96.485335 \text{ kJ mol}^{-1}$
Foot	$1 \text{ ft} = 12 \text{ in} = 0.3048 \text{ m}$ (exactly)
Gallon (U. S.)	$1 \text{ gallon} = 4 \text{ quarts} = 3.785412 \text{ L}$ (exactly)
Liter	$1 \text{ L} = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3$ (exactly)
Liter-atmosphere	$1 \text{ L atm} = 101.325 \text{ J}$ (exactly)
Metric ton	$1 \text{ t} = 1000 \text{ kg}$ (exactly)
Pound	$1 \text{ lb} = 16 \text{ oz} = 0.4539237 \text{ kg}$ (exactly)
Rydberg	$1 \text{ Ry} = 2.17987197 \times 10^{-18} \text{ J} = 1312.7136 \text{ kJ mol}^{-1} = 13.60569193 \text{ eV}$
Standard atmosphere	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$ (exactly)
Torr	$1 \text{ torr} = 133.3224 \text{ Pa}$



Numbers in parentheses are mass numbers of radioactive isotopes.

[illegible]

Claim Form for General Chemistry Examination

Page (/)

Class: _____, Professor Name: _____, I.D.# : _____, Name: _____

If you have any claims on the marked paper, please write down them on this form and ***submit this with your paper in the assigned place.*** (And this form should be attached ***on the top of the marked paper with a stapler.***) Please, ***copy this***

By Student		By TA	
Question #	Claims	Accepted? Yes(✓) or No(✓)	
		Yes: <input type="checkbox"/>	No: <input type="checkbox"/>
		Pts (+/-)	Reasons

sheet if you need more before use.

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	4+2/6	7	3+3+3/9	/100
2	3+4/7	8	3+4/7	
3	3+6/9	9	3+3+1/7	
4	3+3/6	10	3+3+3/9	
5	2x3+3+3/12	11	2x5/10	
6	3+3+4/10	12	4+4/8	

Missing units in the answer: -1 pt, “-1 pt” means “minus 1 point”

1. (Total 6 pts)

(a) (4 pts) **P_{air} 2 pts, P_{unknown} 2 pts**

The chemical amount of air that was present in the 6.00 L portion of air mixed with the vapors of the unknown can be computed because its physical state after purification is fully described. Assuming ideality

$$n_{\text{air}} = \frac{PV}{RT} = \frac{(1.000 \text{ atm})(3.75 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(223.15 \text{ K})} = 0.2048 \text{ mol}$$
$$P_{\text{air}} = \frac{n_{\text{air}}RT}{V}$$
$$P_{\text{air}} = \frac{(0.2048 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(298.15 \text{ K})}{6.00 \text{ L}} = 0.835 \text{ atm}$$

But the total pressure above the unknown was 0.980 atm. By Dalton's law

$$P_{\text{unknown}} = 0.980 - 0.835 = 0.145 \text{ atm}$$

(b) (2 pts) **each liquid 1 pt**

The unknown liquid has a vapor pressure of 0.145 atm at 25 °C. Thus its vapor pressure curve lies between those of water and diethyl ether. Therefore, **water and diethyl ether** have the boiling points closest to the unknown liquid.

2. (Total 7 pts)

(a) (3 pts)

CCl_3F is a polar molecule (strong dipole-dipole forces)

We expect that CCl_3F will have the highest T_c .

The remaining 3 substances can interact only by way of induced dipole-dipole (London dispersion force)

We would predict T_c to decrease in the order Kr (36 electrons), Ar (18 electrons), and H_2 (2 electrons).

(b) (4 pts) each 2 pts

(1) London forces between SO_2 molecules should be greater than CO_2 .

Moreover, as SO_2 is polar but CO_2 is not.

Therefore SO_2 has the lower vapor pressure.

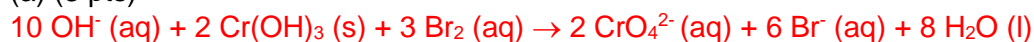
(2) Molecular weights are equal.

However, there will be strong hydrogen bonding in ethanol.

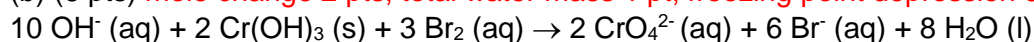
We expect **ethanol** to have the lower vapor pressure.

3. (Total 9 pts)

(a) (3 pts)



(b) (6 pts) mole change 2 pts, total water mass 1 pt, freezing point depression 3 pts



2 mol	1 mol	0.3 mol			
-1 mol	-0.2 mol	-0.3 mol	+0.2 mol	+0.6 mol	+0.8 mol
1 mol	0.8 mol	0 mol	0.2 mol	0.6 mol	0.8 mol

After the reaction, 2 mol $\text{Na}^+(\text{aq})$ + 1 mol $\text{OH}^-(\text{aq})$ + 0.2 mol $\text{CrO}_4^{2-}(\text{aq})$ + 0.6 mol $\text{Br}^-(\text{aq})$ = 3.8 moles of solute are left in the aqueous phase. Total water mass is 1 kg + (0.8 mol)*(15.999+1.008*2 g/mol)*(1/1000 kg/g) = 1.014 kg.

Use these to calculate the freezing point depression of

$$\Delta T_f = -K_f \cdot m = -(1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \cdot (3.8 \text{ mol} / 1.014 \text{ kg}) = -6.97 \text{ K}$$

Thus, the freezing point of this solution mixture after the reaction is **-6.97 °C**.

4. (Total 6 pts)

(a) (3 pts)

At 624 °C, both liquid and solid are at equilibrium and the liquid is denser. Therefore, when it is compressed at the same temperature, the equilibrium will shift to the denser side and the solid will melt. Namely, the melting point lowers. At 625 °C (above melting point), plutonium will exist as liquid, and as it gets compressed, the melting point will lower. Thus, because the maintained temperature will be higher than the melting temperature and the sample will **remain in the liquid state**. (No change will happen.)

(b) (3 pts)

At lower temperature: solid \rightarrow either (1) or (3); melting point lowers at higher pressure \rightarrow (3) or (4).

Therefore, **(3) is the right shape**.

5. (Total 12 pts)

(a) (2 pts)

$$P = 17.5 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.023 \text{ atm}$$

$$V = 1\text{L}, T = 20^\circ\text{C} = 293 \text{ K}, R = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

$$n = \frac{PV}{RT} = \underline{9.57 \times 10^{-4} \text{ mol}}$$

(b) (2 pts)

The same as in a 1L container: 17.5 torr

The vapor pressure depends only on temperature.

(c) (2 pts)

Since the volume doubles, so must the number of moles.

$$9.57 \times 10^{-4} \text{ moles} \times 2 = \underline{1.91 \times 10^{-3} \text{ mol}}$$

(d) (3 pts)

$$P = 9.2 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.012 \text{ atm}$$

$$V = 1\text{L}, T = 10^\circ\text{C} = 283 \text{ K}$$

$$n = \frac{PV}{RT} = \frac{0.012 \times 1}{0.082 \times 283} = 5.2 \times 10^{-4} \text{ mol}$$

$$9.57 \times 10^{-4} \text{ mol} - 5.2 \times 10^{-4} \text{ mol} = 4.4 \times 10^{-4} \text{ mol}$$

The difference, $4.4 \times 10^{-4} \text{ mol}$, condensate

$$4.4 \times 10^{-4} \text{ mol} \times \frac{18\text{g}}{\text{mol}} \times \frac{1\text{mL}}{1\text{g}} = \underline{7.9 \times 10^{-3} \text{ mL}}$$

(e) (3 pts)

$$n_1 = 500\text{g H}_2\text{O} \times \frac{1 \text{ mol}}{18\text{g}} = 27.8 \text{ mol H}_2\text{O}$$

$$X_1 = \frac{n_1}{n_1 + n_2} \quad X_1(n_1 + n_2) = n_1$$

$$n_2 = \frac{n_1(1 - X_1)}{X_1}$$

$$P_1 = X_1 P_1^0$$

$$X_1 = \frac{P_1}{P_1^0} = \frac{16.1 \text{ torr}}{17.5 \text{ torr}} = 0.92$$

$$n_2 = \frac{n_1(1 - X_1)}{X_1} = \frac{(27.8)(1 - 0.92)}{0.92} = 2.47 \text{ mol}$$

$$\text{molality} = \frac{2.47 \text{ mol sucrose}}{0.5 \text{ kg H}_2\text{O}} = \underline{4.83 \text{ m}}$$

6. (Total 10 pts)

(a) (3 pts)

a) The equation is $\boxed{\text{C}_{10}\text{H}_8(s) + 12 \text{O}_2(g) \longrightarrow 10 \text{CO}_2(g) + 4 \text{H}_2\text{O}(l)}$.

(b) (3 pts)

b) The amount of heat evolved ($-q$) in the combustion of 0.6410 g of naphthalene was observed to equal 25.79 kJ. Since the combustion was performed at constant volume, no work was done on the system ($w = 0$). Therefore, $\Delta U = q + w = -25.79 \text{ kJ} + 0 = -25.79 \text{ kJ}$. Put this ΔU on a molar basis to correspond to the 1 mol of naphthalene appearing in the balanced equation

$$\Delta U = \left(\frac{-25.79 \text{ kJ}}{0.6410 \text{ g C}_{10}\text{H}_8} \right) \times \left(\frac{128.17 \text{ g C}_{10}\text{H}_8}{1 \text{ mol C}_{10}\text{H}_8} \right) = -5157 \text{ kJ mol}^{-1}$$

The temperature is 25°C both before and after the reaction. Therefore for the equation written above (which shows 1 mol of naphthalene) $\Delta U^\circ = \boxed{-5157 \text{ kJ}}$.

(c) (4 pts)

c) To calculate ΔH° use the definition

$$\Delta H^\circ = \Delta U^\circ + \Delta(PV)$$

Assume that the gases are ideal and that the volumes of the solids are negligible. Then $\Delta(PV) = (\Delta n_g)RT$, and

$$\Delta H^\circ = \Delta U^\circ + (\Delta n_g)RT$$

The Δn_g is the change in the number of moles of gases during the reaction. The combustion of 1 mol of naphthalene produces 10 mol of gas, while consuming 12 mol of gas. Accordingly

$$(\Delta n_g)RT = (-2 \text{ mol})(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(298.15 \text{ K}) = -4.96 \text{ kJ}$$

$$\Delta H^\circ = \Delta U^\circ + (\Delta n_g)RT = -5157 \text{ kJ} - 4.96 \text{ kJ} = \boxed{-5162 \text{ kJ}}$$

7. (Total 9 pts)

(a) (3 pts)

Initially, $n = 2.00 \text{ mol}$, $P_0 = 3.00 \text{ atm}$, $T_0 = 350 \text{ K}$. Thus, $V_0 = nRT/P = 19.1 \text{ L}$.

After expansion, $V = 2V_0 = \mathbf{38.3 \text{ L}}$.

(b) (3 pts)

$w = -P_{\text{ext}} \Delta V = -1.00 \text{ atm} * 19.1 \text{ L} = -101325 \text{ Pa} * 0.0191 \text{ m}^3 = -1940 \text{ J}$.

Because the process is adiabatic, $\Delta U = w = \mathbf{-1940 \text{ J}}$.

(c) (3 pts)

For monatomic ideal gas, $\Delta U = \frac{3}{2}nR\Delta T$. Therefore, $\Delta T = -77.8 \text{ K}$, and the final temperature is $\mathbf{272 \text{ K}}$.

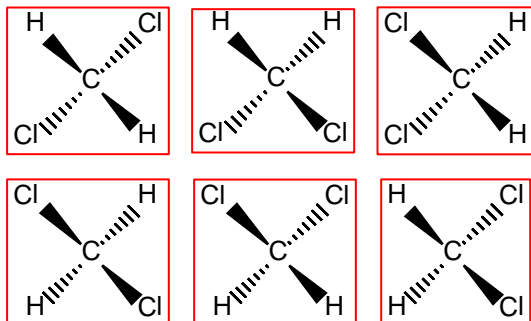
8. (Total 7 pts)

(a) (3 pts)

$$S = k_B \ln 2^{N_A} = k_B N_A \ln 2 = 5.76 \text{ J/K}$$

(b) (4 pts) 6 orientations 2 pts; entropy 2 pts

There are six orientations of CH_2Cl_2 molecule as shown below:



$$S = k_B \ln 6^{N_A} = k_B N_A \ln 6 = 14.90 \text{ J/K}$$

9. (Total 7 pts) ΔS_{sys} 3 pts, ΔS_{surr} 3 pts, ΔS_{tot} 1 pt

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Since S is a function of state, ΔS_{sys} for the irreversible process is equal to ΔS_{sys} for the reversible process with the same initial and final states.

$$\begin{aligned} \text{Thus, } \Delta S_{\text{sys}} &= q_{\text{rev}}/T = -w/T = [-nRT \ln (V_2/V_1)]/T = [-nRT \ln (P_1/P_2)]/T = nR \ln (P_1/P_2) \\ &= (5.00 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \ln (10.0 \text{ atm}/1.00 \text{ atm}) \\ &= 95.7 \text{ J K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{surr}} &= (\text{heat given up by the surrounding})/T = -(\text{heat absorbed by the system})/T \\ &= -q_{\text{irrev}}/T = -(-w_{\text{irrev}})/T = (w_{\text{irrev}})/T = -P_{\text{ext}}\Delta V/T = -(1 \text{ atm})(V_f - V_i)/T \end{aligned}$$

$$V_i = nRT/P_i = (5.00 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})/10.0 \text{ atm} = 12.2 \text{ L}$$

$$V_f = nRT/P_f = (5.00 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})/1.00 \text{ atm} = 122 \text{ L}$$

Thus,

$$\begin{aligned} \Delta S_{\text{surr}} &= -(1 \text{ atm})(V_f - V_i)/T = - (1 \text{ atm})(122 \text{ L} - 12.2 \text{ L})/298 \text{ K} = - (109.8 \text{ L atm})/298 \text{ K} \\ &= - (109.8 \text{ L atm})(101.3 \text{ J/L atm})/298 \text{ K} = - 37.3 \text{ J K}^{-1} \end{aligned}$$

$$\text{Hence, } \Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 95.7 \text{ J K}^{-1} + (- 37.3 \text{ J K}^{-1}) = 58.4 \text{ J K}^{-1}$$

10. (Total 9 pts)

(a) (3 pts)

$$\Delta G^\circ / (\text{kJ/mol}) = 4 * 51.29 + 6 * (-228.59) - 4 * (-16.48) - 7 * 0 = -1100.46$$

From $\Delta G = \Delta G^\circ + RT^\circ \ln Q = 0$, when $Q = K$, we get

$$K = \exp\left(-\frac{\Delta G^\circ}{RT^\circ}\right) = 6.2 \times 10^{192}.$$

(b) (3 pts)

At 25°C,

$$\Delta H^\circ / (\text{kJ/mol}) = 4 * 33.18 + 6 * (-241.82) - 4 * (-46.11) - 7 * 0 = -1133.76$$

$$\Delta S^\circ = -\frac{\Delta G^\circ - \Delta H^\circ}{T^\circ} = -111.7 \text{ J/mol} \cdot \text{K}$$

Therefore, at $T = 273.15 \text{ K}$,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -1103.25 \text{ kJ/mol}$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = 9.3 \times 10^{210}.$$

(c) (3 pts)

$$\Delta S^\circ / (\text{J/K mol}) = 4 * 239.95 + 6 * 188.72 - 4 * 192.34 - 7 * x = -111.7$$

Therefore, $x = 204.9$ and the standard entropy is **204.9 J/K·mol**.

$$\begin{aligned} * \exp(443.9) &= \exp(192.8 * \ln 10) = (\exp(\ln 10))^{192.8} = 10^{192.8} = 10^{0.8} * 10^{192} \\ &= 6.3 * 10^{192} \end{aligned}$$

11. (Total 10 pts) for each, 2 pts

Chemical systems always tend toward equilibrium.² If a stress is applied to a system at equilibrium, the system reacts to minimize the stress and to reach a new equilibrium.

a) The stress is the addition of $\text{N}_2\text{O}(g)$. The system reacts to decrease the concentration of N_2O . The reaction proceeds from **right to left** until a new equilibrium is reached.

b) The stress is the reduction in volume. The partial pressures of all the compounds will momentarily rise. The equilibrium will then shift in such a way as to reduce the number of molecules of gas (chemical amount of gas) in the container and reduce the total pressure. There are three moles of gas on the reactant side of the equation and two moles of gas on the product side. The equilibrium will thus shift from **left to right**.

c) The reaction is exothermic. Cooling the mixture shifts the equilibrium from **left to right** (to favor the products).

d) In order to maintain a constant pressure, the volume of the system must have increased. Thus, the reaction will shift from **right to left**.

e) The partial pressures of the reacting gases are unchanged by the addition of an inert gas, and the equilibrium law is independent of total pressure. There is **no effect** on the position of the equilibrium.

12. (Total 8 pts)

(a) (4 pts) **K 3 pts, backward 1 pt**

$$\ln K = -\Delta G^\circ / RT = -113.63 \times 1000 \text{ J mol}^{-1} / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) = -45.86$$

$$\therefore K = 1.21 \times 10^{-20}$$

Because Equilibrium constant is smaller than one, it is **backward favored** at 298K.

(b) (4 pts) **K 3 pts, forward 1 pt**

Let equilibrium constant K_1 for 25 °C(298K), and K_2 for 1000K

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= \Delta H^\circ_{\text{formation}}(\text{product}) - \Delta H^\circ_{\text{formation}}(\text{reactant}) \\ &= [(-393.5 \text{ kJ/mol}) \times 1\text{mol} + (0 \text{ kJ/mol}) \times 3\text{mol}] - [(-74.9 \text{ kJ/mol}) \times 1\text{mol} + (-241.8 \text{ kJ/mol}) \times 2\text{mol}] \\ &= 165 \text{ kJ}\end{aligned}$$

Let the reaction is proceeded for 1mol CO_2 (g). Then $\Delta H^\circ_{\text{reaction}}$ can be considered as 165 kJ/mol.

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = -\frac{165 \text{ kJ/mol}}{8.314 \text{ J/K mol}} \left[\frac{1}{1000 \text{ K}} - \frac{1}{298 \text{ K}} \right] = 46.75$$

$$\therefore K_2 = K_1 \times e^{46.75} = 2.4324$$

New equilibrium constant is larger than one. Therefore, it is **forward favored** at 1000K.