

Chemistry I -- Final Exam (總分110分)

2013/1/18

Periodic Table of Elements

1 H 1.0																2 He 4.0	
3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 40.0
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)

Formulae

$$PV = nRT = \frac{nMv_{rms}^2}{3}$$

$$\left(P + a \left(\frac{n}{V} \right)^2 \right) (V - nb) = nRT$$

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}}$$

$$E_n = \frac{-Z^2 h R}{n^2}, \quad n = 1, 2, 3, \dots$$

$$R = \frac{m_e e^4}{8h^3 \epsilon_0^2} = 3.29 \times 10^{15} \text{ Hz}$$

Constants

$$\begin{aligned} R &= 8.314 \text{ J / mol K} \\ &= 0.0821 \text{ L atm / K mol} \\ &= 8.314 \text{ L kPa / K mol} \end{aligned}$$

$$1 \text{ atm} = 760 \text{ Torr} = 1.01 \times 10^5 \text{ Pa}$$

$$c = 2.99 \times 10^8 \text{ m/s}$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\text{Mass of } e, m_e = 9.10939 \times 10^{-31} \text{ kg}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

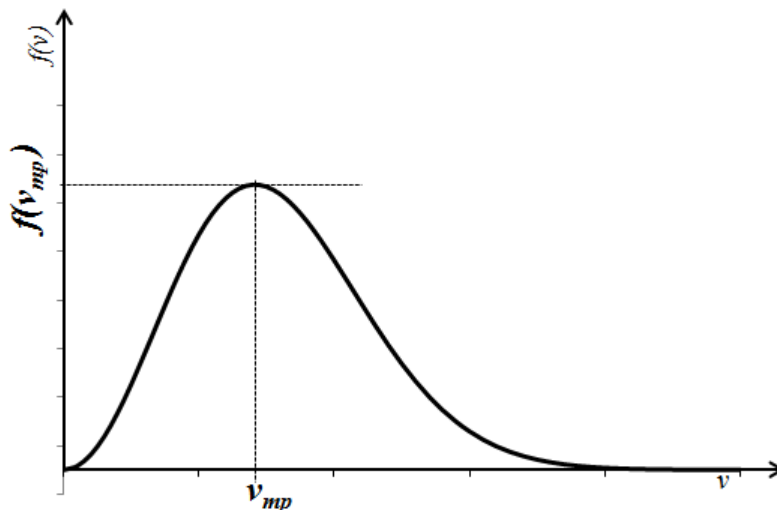
$$\text{Avagadro number, } N_A = 6.022 \times 10^{23}$$

1. (9 % total) In a closed system 1.0 L of monatomic ideal gas in a volume-flexible container was heated from $T = -20\text{ }^\circ\text{C}$ and $P = 759\text{ Torr}$ to $T = 255\text{ }^\circ\text{C}$, then the pressure was increased to 865 Torr. Finally it was heated again to $850\text{ }^\circ\text{C}$ at the same time the pressure was decreased to 300 Torr. (a) What is the final volume of the gas? (2 %) (b) What is the total enthalpy change of this process (ΔH)? (7 %)

2. (10 % total) In the kinetic model of gases, the molecules are widely separated for most of the time and in ceaseless random motion. Assuming that the system is ideal gas under thermal equilibrium and Maxwell distribution of speeds can be represented by the following equation:

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}$$

The graph of the Maxwell distribution function $f(v)$ is drawn below



- (a) Find the most probable speed v_{mp} . (5 %)
 (b) Determine the Maxwell distribution function as a function of v_{mp} . (5 %)

3. (6% total) The van der Waals equation and compression factor can be expressed as

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad \text{and} \quad Z = \frac{V_m}{V_m^{\text{ideal}}}$$

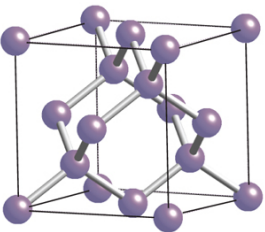
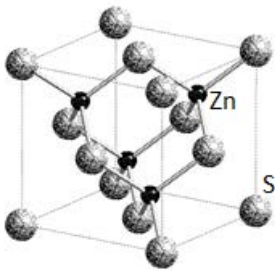
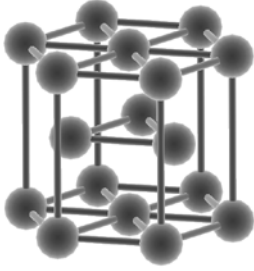
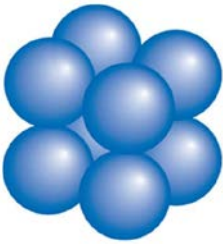
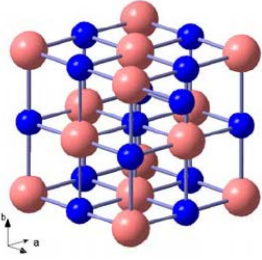
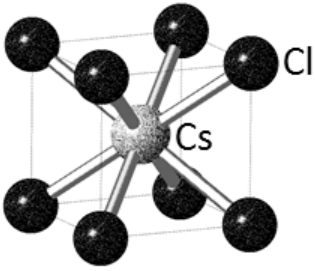
, where V_m represents the molar volume. At low pressure, what are the values of a and b for (i) $Z = 1$ (1%); (ii) $Z > 1$ (1%); (iii) $Z < 1$ (1%), and explain the physical meaning of these three situations. (3%)

4. (10% total) Identify and give the most important intermolecular forces that exist or dominate in the followings.

- (a) Inert gas argon crystallizes into a solid at low temperature. (2%)
- (b) Molecules of octadecane ($C_{18}H_{38}$) form a waxy solid. (2%)
- (c) Dissolution of $NaNO_3$ in water and form hydrated ions. (2%)
- (d) Molecules of $CHCl_3$ crystallize in the solid state. (2%)
- (e) The vapor of acetic acid that contains dimer. (2%)

5. (6% total) Consider the following crystal structures for various solids.

- (a) Which of the following structure types is NOT a closed-packed structure? (2%)
- (b) Which structure(s) has all its octahedral holes occupied? (2%)
- (c) Which structure(s) contains ions with coordination number eight? (2%)

<p>(A) Diamond</p> 	<p>(B) Sphalerite</p> 	<p>(C) Zinc</p> 
<p>(D) Simple cubic</p> 	<p>(E) Rock salt</p> 	<p>(F) Cesium chloride</p> 

6. (18% total)

The measured density of rhodium (Rh) metal is $12.42 \text{ g}\cdot\text{cm}^{-3}$ and its atomic radius is 134 pm . Is the rhodium metal closed-packed or body-center cubic?(13%) Why the computed density is not exactly equal to the experimental value? (5%)

7. (10%) A mixture of 1 mole of hydrogen and 1 mole of oxygen react at 25°C in a thermal insulation system under constant pressure; the product is water. Compute the final temperature of the products. You may need the following data:

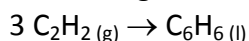
$$\Delta H^\circ_f[\text{H}_2\text{O}(\text{l})] = -285.83 \text{ kJ}\cdot\text{mol}^{-1}, \quad C_{p,m}[\text{H}_2\text{O}(\text{l})] = 75.29 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \quad C_{p,m}[\text{H}_2\text{O}(\text{g})] = 33.58 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$C_{p,m}[\text{H}_2(\text{g})] = 28.82 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \quad C_{p,m}[\text{O}_2(\text{g})] = 29.36 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \quad \Delta H^\circ_{\text{vap}}[\text{H}_2\text{O}(\text{l})] = 40.70 \text{ kJ}\cdot\text{mol}^{-1}$$

You can assume that the heat capacity does not change with temperature.

8. (7%) Derive the equation for the work of reversible, isothermal expansion of ideal gas.

9. (8%) Compute the standard enthalpy of the following reaction



knowing that:

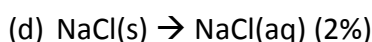
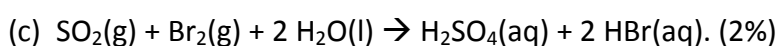
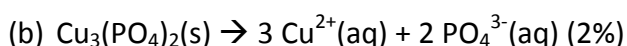
$$\Delta H^\circ_{\text{comb}}[\text{C}_2\text{H}_2(\text{g})] = -1300 \text{ kJ}\cdot\text{mol}^{-1}, \quad \Delta H^\circ_{\text{comb}}[\text{C}_6\text{H}_6(\text{l})] = -3268 \text{ kJ}\cdot\text{mol}^{-1}, \quad \Delta H^\circ_f[\text{H}_2\text{O}(\text{l})] = -286 \text{ kJ}\cdot\text{mol}^{-1}, \quad \text{and}$$

$$\Delta H^\circ_f[\text{CO}_2(\text{g})] = -394 \text{ kJ}\cdot\text{mol}^{-1}.$$

10. (12%) Suppose 24.0 g carbon dioxide, $\text{CO}_2(\text{g})$, is heated reversibly from 300K to 600 K at a constant volume of 20.0 L (Path A), and then allowed to expand isothermally and reversibly until the original pressure is reached (Path B). Using $C_p(\text{CO}_2(\text{g})) = 37.1 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU , ΔH , and ΔS for paths A and B. Assume that $\text{CO}_2(\text{g})$ is an ideal gas under these conditions.

11. (6%) A sample of ethanol ($\text{C}_2\text{H}_5\text{OH}$) is heated to its boiling point with the use of a 600 W (1 W = 1 J/s) heater. Once the boiling point is reached, heating continues for 3.0 min and some ethanol molecules are vaporized. After 3.0 min, the sample is cooled and the mass of the remaining liquid is determined. The process is performed at constant pressure. Calculate ΔS_{vap} and ΔH_{vap} for ethanol. Assume that all the heat from the heater goes into the sample. Use the following data, b.p. (ethanol) = 78.3 °C, initial mass (g) = 300.0, and final mass(g) = 184.29.

12. (8% total) Predict whether there is an increase or a decrease in entropy for each of the following processes. Explain your reasoning.



Answers:

1. (9% total)

(a) (2%)

$$\frac{(759 \text{ Torr})(1.00 \text{ L})}{253 \text{ K}} = \frac{(300 \text{ Torr})(V)}{1123 \text{ K}}$$

$$V = 11.23 \text{ L}$$

(b) (7%) 如果計算答案正確，即可直接得 7 分。

$$\Delta H = n C_{p,m} \Delta T$$

$$\Rightarrow \Delta H = \frac{\left(\frac{759 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(1.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(253 \text{ K})} \times \frac{5}{2} (8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times (870 \text{ K})$$
$$= 870 \text{ J (or 0.87 kJ)}$$

如果答案計算錯誤，請依照下列規則給分：

i. (4%)

$$H \equiv U + PV = U + nRT$$

$$\Delta H = \Delta U + nR\Delta T = nC_{v,m}\Delta T + nR\Delta T = (nC_{v,m} + nR)\Delta T = nC_{p,m}\Delta T$$

ii. (2%) Because H is a state function, ΔT is determined by only the initial and final values.

2. (10% total)

(a) (5%)

$$\frac{d f(v)}{dv} = \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mv^2}{2RT}} \left[8\pi v + 4\pi v^2 \left(\frac{-Mv}{RT}\right)\right] = 0$$

Solving for v gives the most probable speed in terms of M , R and T .

$$v_{\text{mp}} = \left(\frac{2RT}{M}\right)^{1/2}$$

(b) (5%)

Substitution of v_{mp} into $f(v)$ would give

$$f(v_{\text{mp}}) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \left(\frac{2RT}{M}\right)^{1/2} \cdot e^{-1} = 4\pi \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-1}$$

3. (6% total)

$$Z = \frac{V_m}{V_m^{\text{ideal}}} = \frac{V/n}{RT/P} = \frac{PV}{nRT} = \frac{V}{V-nb} - \frac{an}{VRT} = \frac{1}{1-\frac{nb}{V}} - \frac{a}{nVRT}$$

(a) $Z = 1$ when $a = b = 0$. (1%) This is the case of ideal gas. (1%)

(b) $Z > 1$ if a is small and b is large. (1%) b is dominant \rightarrow repulsion force between molecules (1%)

(c) $Z < 1$ if b is small and a is large. (1%) a is dominant \rightarrow attraction force between molecules (1%)

4. (10% total)

- (a)(2%) London dispersion forces or London forces or dispersion forces
- (b)(2%) London dispersion forces or London forces or dispersion forces
- (c)(2%) Ion-dipole interaction
- (d)(2%) Dipole-dipole interaction
- (e)(2%) Hydrogen bonding.

5. (6% total)

- (a) (2%) A, B, D, E, F
- (b) (2%) E
- (c) (2%) F

6. (18% total)

(I) Let's assume that Rh metal structure is **ccp (fcc)**. In **ccp** structure, there are 4 atoms in each unit cell. The atomic mass (M) of rhodium is 102.91 g/mol.

Therefore, the density of rhodium is: **(5%)**

$$\begin{aligned}d &= m/a^3, m = \text{mass of one unit cell} = 4M/N_A, a \\ &= \text{the length of the side of a fcc unit cell} = 8^{1/2}r \\ d &= \frac{4M / N_A}{(8^{1/2}r)^3} = \frac{4M}{N_A(8^{1/2}r)^3} \\ &= \frac{4 \text{ atoms} \times (102.91 \text{ g} \cdot \text{mol}^{-1})}{(6.022 \times 10^{23} \text{ atom} \cdot \text{mol}^{-1}) \times (8^{1/2} \times 1.34 \times 10^{-8} \text{ cm})^3} = 12.55 \text{ g} \cdot \text{cm}^{-3}\end{aligned}$$

(II) Then, we assume that the Rh metal structure is **bcc**. In **bcc** structure, there are 2 atoms in each unit cell, and

a = the length of the side of a **bcc** unit cell = $4r/3^{1/2}$. The density of Rh is:

$$\begin{aligned}d &= \frac{2M / N_A}{(4r/3^{1/2})^3} = \frac{2M}{N_A(4r/3^{1/2})^3} \\ &= \frac{2 \text{ atoms} \times (102.91 \text{ g} \cdot \text{mol}^{-1})}{(6.022 \times 10^{23} \text{ atom} \cdot \text{mol}^{-1}) \times (4 \times 1.34 \times 10^{-8} \text{ cm} / 3^{1/2})^3} = 11.53 \text{ g} \cdot \text{cm}^{-3}\end{aligned}$$

(5%)

The density value for the **ccp** structure is closer to $12.42 \text{ g} \cdot \text{cm}^{-3}$.

Therefore, Rh metal is close-packed structure. (3%)

第二部分的答案是開放，且比較彈性給分。以下任意答案皆可以得滿分**(5%)**

- i. 晶體可能有缺陷
- ii. 晶體中有空隙或氣泡
- iii. 原子半徑不夠精準

7. (10% total)

The products of the reaction are the mixture of 1 mole of H₂O and ½ mole of O₂. The energy produced in the reaction is equal to 285830 J. **(2%)**

This energy is used to heat the final products to the final temperature. The heating can be divided in three stages:

(i) heating both products from 25°C to 100°C.

$$Q = \Delta T \cdot (C_{p,m}[\text{H}_2\text{O}(\text{l})] + C_{p,m}[\text{O}_2(\text{g})]/2) = 75 \cdot (75.29 \cdot 1 + 29.36 \cdot 0.5) = 6747.75 \text{ J} \quad \mathbf{(3\%)}$$

(ii) vaporization of water from liquid phase to gas phase

$$Q = \Delta H^\circ_{\text{vap}}[\text{H}_2\text{O}(\text{l})] \cdot 1 = 40.70 \text{ kJ} = 40700 \text{ J} \quad \mathbf{(2\%)}$$

(iii) heating both products from 100°C to the final temperature T.

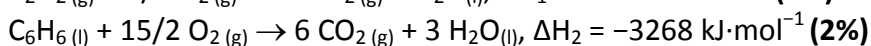
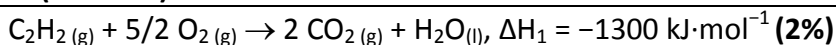
$$T = 100 + (285830 - 6747.75 - 40700) / (C_{p,m}[\text{H}_2\text{O}(\text{g})] + C_{p,m}[\text{O}_2(\text{g})]/2)$$

$$T = 100 + (285830 - 6747.75 - 40700) / (33.58 \cdot 1 + 29.36 \cdot 0.5) = 5039.536^\circ\text{C} \approx 5040^\circ\text{C} \quad \mathbf{(3\%)}$$

8. (7% total)

$dw = -p_{\text{ext}} \cdot dV$ (standard formula for expansion work); the process is reversible, so $p_{\text{ext}} = p_{\text{int}} = p$, so $dw = -p \cdot dV$; the gas is ideal so $p = n \cdot R \cdot T / V$; this gives $dw = -n \cdot R \cdot T / V \cdot dV$; integrating this from V_1 to V_2 gives $p = \int_{V_1}^{V_2} -nRT/V dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_1}{V_2}$ **(7%)**

9. (8% total)



Summing both equations with coefficients 3 and -1 gives the final result $\Delta H = -632 \text{ kJ} \cdot \text{mol}^{-1}$ **(4%)**

10. (12% total)

CO₂ 24g → 0.5 mole

$$C_p = 37.11 \text{ J K}^{-1} \text{ mol}^{-1} = C_v + R \rightarrow C_v = 37.11 - 8.314 = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Path A: 300 – 600 K, const V, $dV = 0$

$$w_A = 0$$

$$q_A = n \times C_v \times \Delta T = 0.5 \times 28.8 \times (600 - 300) = 4320 \text{ J}$$

$$\Delta U_A = q_A + w_A = q_A = 4320 \text{ J} \quad \text{-----}>\mathbf{(2\%)}$$

$$\Delta H_A = n \times \Delta T \times C_p = 0.5 \times 300 \times 37.11 = 5565 \text{ J} \quad \text{-----}>\mathbf{(2\%)}$$

$$\Delta S_A = n \int \frac{dq_{\text{rev}}}{T} = n \int \frac{C_v dT}{T} = n C_v \ln \left(\frac{T_2}{T_1} \right) = n C_v \ln \left(\frac{600}{300} \right)$$

$$= 0.5 \times 28.8 \times \ln(2) = 9.98 \text{ J/K} \quad \text{-----}>\mathbf{(2\%)}$$

Path B: isothermal expansion, $dT = 0$

$$\Delta U_B = 0 = q_B + w_B = 0 \quad \text{-----}>\mathbf{(2\%)}$$

$$\Delta H_B = \Delta U_B + \Delta(PV) = \Delta U_B + \Delta(nRT) = \Delta U_B + nR\Delta T = 0 \quad \text{-----}>\mathbf{(2\%)}$$

$$\Delta S_B = nR \ln \left(\frac{V_2}{V_1} \right) = nR \ln \left(\frac{T_2}{T_1} \right) = 0.5 \times 8.314 \times \ln(600/300) = 2.88 \text{ J/K} \quad \text{-----}>\mathbf{(2\%)}$$

or

$$w_B = -nRT \ln \left(\frac{V_2}{V_1} \right) = -nRT \ln \left(\frac{T_2}{T_1} \right) = -0.5 \times 8.314 \times 600 \times \ln(600/300) = -1728.8 \text{ J}$$

$$q_B = -w_B = 1728.8 \text{ J}$$

$$\Delta S_B = q_B/T = (1728.8/600) = 2.88 \text{ J/K}$$

11. (6% total)

The molar enthalpy of vaporization is found by dividing the amount of energy supplied to cause the phase transition by the number of moles of C_2H_5O that underwent the transition:

$$\Delta H_{vap} = \frac{(600 \text{ J} \cdot \text{s}^{-1})(3.0 \text{ min})(60 \text{ s} \cdot \text{min}^{-1})}{\left(\frac{300 \text{ g} - 184.29 \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}} \right)} = 43 \text{ kJ} \cdot \text{mol}^{-1} \quad (3\%)$$

The associated change in entropy is then found using:

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{43 \text{ kJ} \cdot \text{mol}^{-1}}{273.15 + 78.3 \text{ K}} = 122.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad (3\%)$$

12. (8% total)

- (a) **(2%)** Decrease: the number of moles of gas is less on the product side of the reaction.
- (b) **(2%)** Increase : the dissolution of the solid copper phosphate will increase the randomness of the copper and phosphate ions.
- (c) **(2%)** Decrease: the total number of moles decreases.
- (d) **(2%)** Increases: The molecules or ions are dispersed in the solvent, giving them more locations over which to arrange themselves.