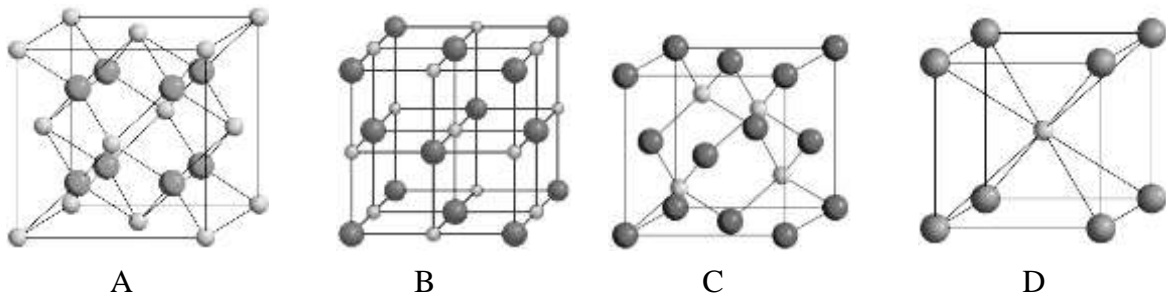




3. (a) What is the dimensionality (degree of freedom) of the three-phase coexistence region in mixture of Al, Ni, and Cu? (b) What type of geometrical region does this define: a point, a line, a surface, or a space? (3+2%)
4. To what temperature must He atoms be cooled so that they have the same root-mean-square (rms) speed as O<sub>2</sub> at 25 °C? (6%)
5. (a) Derive relationships between the van der Waals equation  $P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$  and the virial equation  $\frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \dots$  between the van der Waals constants ( $a$  and  $b$ ) and the virial coefficient  $B$ , given that  $\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots$  for  $|x| < 1$ .  
 (b) Using your results, determine the Boyle temperature for a van der Waals gas in terms of  $a$  and  $b$ . (6+3%)

6.



- (a) Which one is the crystal structure of the NaCl unit cell? (b) How many Na<sup>+</sup> and Cl<sup>-</sup> ions are in each NaCl unit cell? (Please show your calculation.) (3+4%)

7. (a) Explain why we use X-ray (rather than other radiations like UV-vis or IR) to obtain the diffraction patterns from layers of atoms? (b) The distance between layers in a NaCl crystal is 282 pm. X-rays are diffracted from these layers at an angle of 23.0°. Assuming that  $n = 1$  (first order diffraction), calculate the wavelength of the X-rays (in nm). (2+4%)
8. Given that the density of solid CsCl is 3.97 g·cm<sup>-3</sup>, calculate the distance between adjacent Cs<sup>+</sup> and Cl<sup>-</sup> ions. (6%)
9. The reaction of ethylene C<sub>2</sub>H<sub>4</sub> with oxygen is given by the equation:  

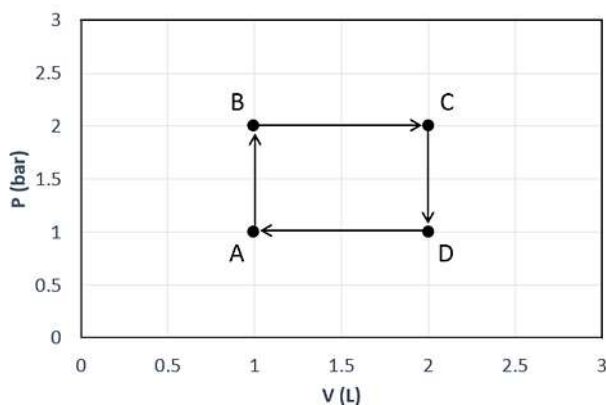
$$\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$$
 Use the thermodynamic data at 25 °C to solve the following problems. Here, all the gases involved in the reaction behave like ideal gases, their molar heat capacities do not contain any

vibrational contributions. Thermodynamic data at 25 °C (assume that  $\Delta H_f^\circ$  and  $S^\circ$  are **independent** of temperature)

	$\Delta H_f^\circ$ (kJ·mol <sup>-1</sup> )	$S^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ·mol <sup>-1</sup> )
C <sub>2</sub> H <sub>4</sub> (g)	52.4	219.3	68.4
C <sub>2</sub> H <sub>2</sub> (g)	227.4	200.9	209.9
CO <sub>2</sub> (g)	-393.5	213.6	-394.4
CO(g)	-110.5	197.9	-137.3
H <sub>2</sub> O(l)	-285.8	69.95	-237.1
H <sub>2</sub> O(g)	-241.83	188.8	-228.6

- (a) Please calculate  $\Delta H_{\text{rxn}}^\circ$  at 25 °C. (3%)
- (b) Please calculate  $\Delta U_{\text{rxn}}^\circ$  at 25 °C. (3%)
- (c) Now, 2 mole of ethylene is put into an adiabatic closed chamber with 3 mole of oxygen gas at 25 °C and the reaction is initiated by a spark. Please predict the final composition of gases, and the final temperature of the chamber when the reaction completes. (7%)

10. Starting at A, one mole of an ideal gas undergoes a cyclic process involving expansion and compression as show below.



Please answer the following questions:

- (a) What is the sign of  $\Delta T(A \rightarrow B)$ ? (+, -, or 0) (2%) Please explain it briefly. (2%)
- (b) What is the sign of  $\Delta U(A \rightarrow B)$ ? (+, -, or 0) (2%) Please explain it briefly. (2%)
- (c) What is the sign of  $q(C \rightarrow D)$ ? (+, -, or 0) (2%) Please explain it briefly. (2%)
- (d) What is the sign of  $\Delta U$  (cycle:  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ )? (+, -, or 0) (2%) Please explain it briefly. (2%)

11. Answer True or False to the following statements. (2% each, 20% total)

- (a) When a liquid is vaporized, the process is endothermic and change of S is positive.

- (b) A negative sign for  $\Delta G$  indicates that, at constant  $T$  and  $P$ , the reaction is exothermic.
- (c) A spontaneous endothermic reaction always causes the surroundings to get colder.
- (d) The reaction  $\text{SiO}_2(\text{s}) + \text{Pb}(\text{s}) \rightarrow \text{PbO}_2(\text{s}) + \text{Si}(\text{s})$  is spontaneous.  
 $\Delta G_f(\text{PbO}_2) = -217 \text{ kJ/mol}$  ;  $\Delta G_f(\text{SiO}_2) = -856 \text{ kJ/mol}$
- (e) For a process at equilibrium, the Gibbs free energy change can be positive or negative.
- (f) When a molecular solid is dissolved in a solvent, the enthalpy of solution can be positive or negative while the Gibbs free energy change is negative.
- (g) For a process with negative  $\Delta H$  and negative  $\Delta S$  values, its  $\Delta G$  must be negative.
- (h) Trouton's rule states that the molar enthalpy of vaporization of different liquids has similar values,  $88 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .
- (i)  $\Delta S = q_{\text{rev}}/T$ .  $S$  is a state function.
- (j) When a spontaneous process is reversed, the reversed process is nonspontaneous.

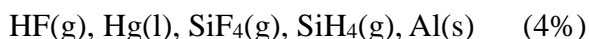
12. By using the following data, calculate  $\Delta H_{\text{rxn}}^\circ$ ,  $\Delta S_{\text{rxn}}^\circ$ , and  $\Delta G_{\text{rxn}}^\circ$  for the reaction. Is the reaction spontaneous at  $25^\circ\text{C}$ ? (9%)



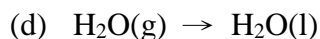
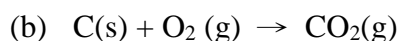
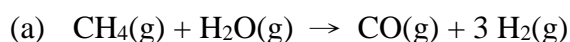
$$\Delta H_f^\circ \text{ of SiH}_4(\text{g}) \text{ is } 34.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(\text{SiH}_4(\text{g})) = 204.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} ; S^\circ(\text{Si}(\text{s})) = 18.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} ; S^\circ(\text{H}_2(\text{g})) = 130.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

13. Arrange the following substances in the order of increasing entropy at  $25^\circ\text{C}$ :



14. Arrange the following reactions according to increasing  $\Delta S$ . (4%)



15. Consider one mole of a monatomic ideal gas in a volume of 25 L and a pressure of 1 bar. The sample is cooled at constant pressure until the volume equals 12.5 L. Then the sample is heated at constant volume to a pressure of 2 bar. Finally, an isothermal expansion of the sample returns it to the original state.

(a) Calculate the entropy change for each one of three steps in the cycle. (6%)

(b) Calculate the total entropy change of the cycle step by step. (4%)

(c) Use the cycle to support the idea that entropy is a state function. (2%)

105A Chemistry (I) Final Exam

Answer

1. 5% , 全對才給分

$$\mu_0 = q (1.0 \text{ \AA}) = 4.8 \text{ D}; \mu(\text{HF}) = \delta \cdot ed = \delta \cdot q (0.917 \text{ \AA})$$

$$\delta = \frac{\mu(\text{HF})}{q (0.917 \text{ \AA})} = \frac{1.92}{\left(\frac{4.8}{1.0}\right) \times 0.917} = 43.6 \%$$

2. 6% , 算式都對但最後答案錯給 3%

$$V = -\frac{\mu_A \mu_B}{4\pi \epsilon_0 r^3} = -\frac{(1.87 \times 3.336 \times 10^{-30})^2}{4 \times 3.14 \times 8.854 \times 10^{-12} \times (4.0 \times 10^{-10})^3} = -5.5 \times 10^{-21} \text{ N}\cdot\text{m}$$

上式 4%

To convert the unit of V into  $\text{kJ}\cdot\text{mol}^{-1}$ ,  $V = (-5.5 \times 10^{-21}) \times (6.02 \times 10^{23}) \times 10^{-3} = -3.3 \text{ kJ}\cdot\text{mol}^{-1}$

上式 2%

3. (a) 3% , 全對才給分 ; (b) 2% , 全對才給分

(a) According to phase rule,  $f = c - r + 2 = 3 - 3 + 2 = 2$

(b) The region of three-phase coexistence forms a two-dimensional surface of the overall phase diagram. 三相共存區的自由度是二，所以形成一個二維的平面

4. 6% , 全對才給分

$$\langle u \rangle_{rms} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3RT}{M}}$$

T is proportional to M when both He and O<sub>2</sub> have the same  $\langle u \rangle_{rms}$ .

$$T_{He} = T_{O_2} \frac{M_{He}}{M_{O_2}} = 298 \times \frac{4}{32} = 37.3 \text{ K}$$

5. (a) 6% , 全對才給分 ; (b) 3% , 全對才給分

$$(a) \frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \dots \text{ from virial equation} \quad (1)$$

$$= \frac{\bar{V}}{\bar{V}-b} - \frac{a}{\bar{V}RT} \text{ from VDW equation}$$

$$= \left[ \frac{1}{1-\left(\frac{b}{\bar{V}}\right)} \right] - \frac{a}{\bar{V}RT} = \left[ 1 + \left(\frac{b}{\bar{V}}\right) + \left(\frac{b}{\bar{V}}\right)^2 + \dots \right] - \frac{a}{\bar{V}RT}$$

$$= 1 + \left(b - \frac{a}{RT}\right) \frac{1}{\bar{V}} + b^2 \left(\frac{1}{\bar{V}}\right)^2 + \dots \quad (2)$$

Compare the coefficients between (1) and (2) we obtain

$$B = b - \frac{a}{RT}$$

(b) The Boyle temperature is defined as  $T = T_B$  when  $B = 0$  (page 321). Therefore,

$$B = b - \frac{a}{RT_B} = 0 \Rightarrow T_B = \frac{a}{Rb}$$

6. (a) 3% ; (b) 4% 沒寫算式但答案對得 2%

(a) structure B

(b) For  $\text{Cl}^-$ ,  $(4+4)/8+6/2 = 4$ ; for  $\text{Na}^+$ ,  $(4+4+4)/4+1 = 4$ .

7. (a) 2% ; (b) 4% , 全對才給分

(a) Because the spacing of the layers of atoms is on the order of  $\sim 1 \text{ \AA}$  (or 100 pm or 0.1 nm), which is in the X-ray region. (or ... is comparable to the X-ray wavelength)

只寫波長短得 1%

(b) According to Bragg equation,

$$2d \sin \theta = n\lambda ; \lambda = \frac{2d \sin \theta}{n} = \frac{2 \times 282 \times \sin 23}{1} = 220 \text{ pm} = 0.22 \text{ nm}$$

8. 6% , 算式對但最後答案錯給 3%

The crystal structure of CsCl is based on body-centered cubic (bcc), and the distance  $r$  between the two ions with respect to the edge length of the lattice  $a$  can be estimated according to the following formula:

$$(2r)^2 = a^2 + b^2 \quad (b^2 = a^2 + a^2) = 3a^2 ; r = \frac{\sqrt{3}}{2} a$$

The density of CsCl  $d$  can be calculated according to the following formula:

$$d = \frac{M}{V} = \frac{168.4}{\frac{6.02 \times 10^{23}}{a^3}} = 3.97$$

$$a^3 = 7.04 \times 10^{-23} ; a = 4.13 \times 10^{-8}$$

$$r = \frac{\sqrt{3}}{2} a = 3.58 \times 10^{-8} \text{ cm (or } 3.58 \text{ \AA or } 358 \text{ pm)}$$

9. (a) 3% ; (b) 3% ; (c) 7% , 共 13%

(a)  $\Delta H_{\text{rxn}}^\circ = (-241.83) \times 2 + (-393.5) \times 2 - (52.4) \times 1 = -1323.1 \text{ kJ}$

(b)  $\Delta U_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - RT\Delta n = -1323.06 - RT \times 0 = -1323.1 \text{ kJ}$

(c) 1 mole of  $\text{C}_2\text{H}_4$  , 2 moles of  $\text{CO}_2$  , 2 moles of  $\text{H}_2\text{O}(\text{g})$  氣體組成答錯一個答案扣 1% , 最多扣 2%

$$-1323.1 \times 10^3 = [\bar{C}_V(\text{C}_2\text{H}_4) \times 1 + \bar{C}_V(\text{CO}_2) \times 2 + \bar{C}_V(\text{H}_2\text{O}) \times 2] \times \Delta T \quad (3\%)$$

$$-1323.1 \times 10^3 = (3R \times 1 + 2.5R \times 2 + 3R \times 2) \times \Delta T = (14 \times 8.314) \times \Delta T$$

$$\Delta T = 11367^\circ\text{C} \quad (1\%) ; T = 25 + 11367 = 11392^\circ\text{C} \quad (1\%)$$

10. (a)-(d) 各 4% , 共 16%

(a) + (2%)

$$\text{Because } T(\text{B}) = \frac{P(\text{B}) \times V(\text{B})}{1 \times R} > T(\text{A}) = \frac{P(\text{A}) \times V(\text{A})}{1 \times R} , \Delta T(\text{A} \rightarrow \text{B}) = T(\text{B}) - T(\text{A}) > 0 \quad (2\%)$$

(b) + (2%)

Because  $\Delta U(A \rightarrow B) = n \times \overline{C_V} \times \Delta T(A \rightarrow B)$  for an ideal gas at constant volume,  $\Delta U(A \rightarrow B) > 0$  (2%)

(c) - (2%)

i  $T(D) = \frac{P(D) \times V(D)}{1 \times R} > T(C) = \frac{P(C) \times V(C)}{1 \times R}$ ,  $\Delta U(C \rightarrow D) = n \times \overline{C_V} \times \Delta T(C \rightarrow D) < 0$

ii  $\Delta U(C \rightarrow D) = q(C \rightarrow D) + w(C \rightarrow D)$

iii Because  $\Delta V(C \rightarrow D) = 0$ ,  $w(C \rightarrow D) = 0$

iv  $q(C \rightarrow D) = \Delta U(C \rightarrow D) - w(C \rightarrow D) < 0$  (2%)

(d) 0 (2%)

Because the initial state is the same as the final state and U is the state function,

$$\Delta U(\text{cycle}; A \rightarrow B \rightarrow C \rightarrow D \rightarrow A) = 0 \quad (2\%)$$

11. (a)-(j) 各 2% , 共 20%

(a) T (b) F (c) T (d) F (e) F

(f) T (g) F (h) F (i) T (j) T

12. 9%

$$\Delta H_{\text{rxn}}^\circ = 1 \text{ mol} \times \Delta H_f^\circ[\text{Si}(s)] + 2 \text{ mol} \times \Delta H_f^\circ[\text{H}_2(\text{g})] - 1 \text{ mol} \times \Delta H_f^\circ[\text{SiH}_4(\text{g})] \quad (1\%)$$

$$= 1 \text{ mol} \times 0 \text{ kJ} \cdot \text{mol}^{-1} + 2 \text{ mol} \times 0 \text{ kJ} \cdot \text{mol}^{-1} - 1 \text{ mol} \times 34.3 \text{ kJ} \cdot \text{mol}^{-1} \quad (1\%)$$

$$= -34.3 \text{ kJ} \quad (1\%)$$

$$\Delta S_{\text{rxn}}^\circ = 1 \text{ mol} \times S^\circ[\text{Si}(s)] + 2 \text{ mol} \times S^\circ[\text{H}_2(\text{g})] - 1 \text{ mol} \times S^\circ[\text{SiH}_4(\text{g})] \quad (1\%)$$

$$= 1 \text{ mol} \times 18.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 2 \text{ mol} \times 130.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - 1 \text{ mol} \times 204.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad (1\%)$$

$$= 75.5 \text{ J} \cdot \text{K}^{-1} \quad (1\%)$$

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ \quad (1\%)$$

$$= -34.3 \text{ kJ} - 298 \text{ K} \times 75.5 / 1000 \text{ kJ} \cdot \text{K}^{-1} = -56.8 \text{ kJ} \quad (1\%)$$

The reaction is spontaneous because  $\Delta G_{\text{rxn}}^\circ$  is negative. (1%)

13. 4%

$\text{Al}(s) < \text{Hg}(l) < \text{HF}(g) < \text{SiH}_4(g) < \text{SiF}_4(g)$

14. 4%

(d) < (b) < (c) < (a)

15. (a) 6% , (b) 4% , (c) 2% , 共 12%

(a) There are three steps in the cycle.

Step 1: T is lowered from  $T_1$  to  $T_2$  causing the volume decrease from 25 L to 12.5 L at constant pressure.

$$\Delta S_1 = C_P \cdot \ln(T_2/T_1) = C_P \cdot \ln(V_2/V_1) = (5R/2) \cdot \ln(12.5/25) = (5R/2) \cdot \ln(1/2) \quad (2\%)$$

Step 2: T is increased from  $T_2$  to  $T_3$  causing the pressure increase from 1 bar to 2 bar at constant volume 12.5 L.

$$\Delta S_2 = C_V \cdot \ln(T_3/T_2) = C_V \cdot \ln(P_3/P_2) = (3R/2) \cdot \ln(2/1) = (3R/2) \cdot \ln 2 \quad (2\%)$$

Step 3: T is the same ( $T_3$ ) while the volume is increased from 12.5 L to 25 L.

$$\Delta S_3 = nR \cdot \ln(V_1/V_3) = 1R \cdot \ln(25/12.5) = R \cdot \ln 2 \quad (2\%)$$

(b) The total entropy change  $\Delta S_{\text{total}}$  is

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 \quad (2\%)$$

$$= (5R/2) \cdot \ln(1/2) + (3R/2) \cdot \ln 2 + R \cdot \ln 2 = (-5/2 + 3/2 + 1) \cdot R \cdot \ln 2 \quad (1\%)$$

$$= 0 \quad (1\%)$$

(c) In the cyclic process, the initial state is the same as the final state. There is no total entropy change as concluded by  $\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 0 \quad (2\%)$