第一部分單選題(1~16)，每題 3 分，請務必使用試卷第一頁[選擇題作答區]作答

1. Which of the following values is closest to the constant pressure heat capacity (in unit of J/mol K) of a monatomic gas such as argon?
(a) 5 (b) 10 (c) 15 (d) 20 (e) 25

2. Effusion, a process in which individual molecules flow through a hole without collisions between molecules, is a simple method for estimation of molecular weight of an ideal gas. The rate of effusion of an unknown gas is 4 times that of oxygen under the same temperature and pressure. What is this gas?
(a) hydrogen (b) helium (c) nitrogen (d) methane (e) carbon dioxide

The volume of an ideal gas is to be compressed to half of its original value. Suppose the constant volume heat capacity of the gas is 50 J/mol K and the initial temperature is 300 K, answer the following questions by choosing one that is closest to the exact solution.

3. What is the change (property in the final state – property in the initial state) in the molar internal energy (kJ/mol) of the gas if the compression is done isothermally at 300 K? (a) -100 (b) -10 (c) 0 (d) 10 (e) 100
4. Following the previous question, what is the minimum work (kJ) required to compress one mole the gas isothermally? (a) 0 (b) 0.3 (c) 0.6 (d) 1.2 (e) 1.8
5. What is the final temperature (K) of the gas if the compression is done adiabatically? (a) 260 (b) 300 (c) 340 (d) 380 (e) 420
6. Following the previous question, what is the minimum work (kJ) required to compress one mole the gas adiabatically? (a) 1.8 (b) 2.0 (c) 2.2 (d) 2.4 (e) 2.6

7. According to the Gibbs' phase rule, what is the maximum number of phases that one may observe for a binary mixture in equilibrium? (a) 1 (b) 2 (c) 3 (d) 4 (e) 5

8. The Henry's law constant of oxygen gas in water is about $4\times10^{4}$atm at room temperature. A glass of water is in equilibrium of air (consisting 20% of oxygen) at room temperature and pressure of 1 atm. What is the equilibrium mole fraction of oxygen in water? (a) $5\times10^{-6}$(b) $1\times10^{-5}$ (c) $5\times10^{-5}$(d) $1\times10^{-4}$ (e) $5\times10^{-4}$

When gaseous $A_2$ is heated, the following reaction occurs: $A_2 \rightleftarrows 2A$. It is found that when 0.006 mole of $A_2$ is placed in a volume of 0.5 liter at 700 K, the degree of dissociation (the fraction of the $A_2$ dissociated) is 0.02.

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9. Which of the following number is closest to Kc, the equilibrium constant? (a) $1\times10^{-6}$ M, (b) $5\times10^{-6}$ M, (c) $1\times10^{-5}$ M, (d) $1\times10^{-4}$ M, (e) $1\times10^{-3}$ M.
10. When the temperature increases to 900 K, which of the following number is closest to Kc? (a) $1\times10^{-7}$ M, (b) $1\times10^{-6}$ M, (c) $5\times10^{-6}$ M, (d) $1\times10^{-5}$ M, (e) $2\times10^{-5}$ M.

11. Given $\Delta_f G^0(O_3, g)$=163.2 kJ/mol. Which of the following number is closest to the equilibrium constant of $3O_2(g) \rightleftarrows 2O_3(g)$ at room temperature? (a)$1\times10^{57}$, (b)$1\times10^{29}$, (c) 1, (d)$1\times10^{-29}$, (e)$1\times10^{-57}$.

12. The pKa values for phosphoric acids are: $pK_1$=2.1 , $pK_2$=7.2, and $pK_3$=12.3. In a solution with $[H^+]=10^{-5}$ M, which of the following species has the highest concentration? (a)$H_3PO_4$ (b)$H_2PO_4^-$ (c)$HPO_4^{2-}$ (d)$PO_4^{3-}$ (e) not possible to determine.

At 25 °C, the electrolytic conductivity of 0.001 M of $Na_2SO_4$ is $2.6\times10^{-4}$ $\Omega^{-1}cm^{-1}$. $\lambda(Na^+)$ is 50 $\Omega^{-1}cm^2\,mol^{-1}$, where $\lambda$ is the molar ionic conductivity.
13. Which of the following statement is correct? (a) The molar conductivity of this solution is 0.26 $\Omega^{-1}cm^2\,mol^{-1}$ (b) $\lambda(\frac{1}{2}SO_4^{2-})$ is 160 $\Omega^{-1}cm^2\,mol^{-1}$ (c) both $\lambda$ and the conductivity change with the vessel geometry (d) the solution resistance changes with the vessel geometry (e) More than one of above statement is correct OR none of the above statement is correct.
14. When this solution is saturated with $CaSO_4$, the conductivity becomes $7\times10^{-4}$ $\Omega^{-1}cm^{-1}$. $\lambda(\frac{1}{2}Ca^{2+})$ is 59.5 $\Omega^{-1}cm^2\,mol^{-1}$. Which of the following number is closest to the solubility product for $CaSO_4$? (a) 4, (b) 6, (c) $4\times10^{-6}$ $M^2$, (d) $2\times10^{-6}$ $M^2$, (e) no enough information to calculate.

15. Which of the following statement is correct? (a) $2NH_3 \rightleftarrows 3H_2 + N_2$ can be an elementary reaction because it only involves the collision between 2 $NH_3$ molecules. (b) For an endothermic reversible reaction, higher temperature gives a higher forward reaction rate and a lower reverse reaction rate. (c) The $T^{1/2}$ dependency of the pre-exponential factor obtained by collision theory is derived from the mean free path of molecules. (d) The addition of catalyst is able to

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change the rate and the equilibrium of a reversible reaction. (e) More than one of the above statements is correct OR none of the above statement is correct.

16. For two exothermic irreversible reactions in parallel: A→ D (1st reaction) and A→ U (2nd reaction), $E_D$ and $E_U$ ($E_D < E_U$) are the activation energy for the 1st and 2nd reactions, respectively, while the reactions are 2nd and 4th order with respect to A for the 1st and 2nd reactions, respectively. Which of the following is correct? (a) High temperature gives a low D formation rate, (b) lower temperature gives a higher D/U formation rate ratio at a constant A concentration, (c) remove of D upon formation gives a higher D formation rate, (d) higher A concentration gives a higher D/U formation rate ratio, (e) more than one of the above statements is correct OR none of the above statement is correct.

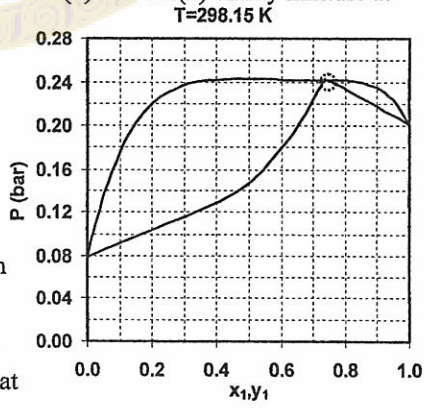
第二部分計算題(17~29)，每題 4 分

17. The first law of thermodynamics states that energy can never be created or destroyed. In this case, why do we have "energy crisis" and need to "save energy"? Answer this question based on the second law of thermodynamics.

The boiling point of compound A is found to be $20^0$C at 1 bar and $10^0$C at 0.5 bar.

18. Determine the heat of vaporization (in kJ/mol) of compound A?
19. If the normal boiling point of A becomes $21^0$C when 1 mole of compound B is added to 1 kg of liquid A, determine the molecular weight (in g/mol) of compound A.

The vapor-liquid equilibrium phase diagram of hexane(1)-ethanol(2) binary mixture at 298K is shown in the figure on the right. As can be seen that the two species form an azeotrope when the mole fraction of hexane is 0.74. Use this figure to answer the following questions.




20. Determine the fugacity of ethanol and hexane, respectively, in the vapor phase at the azeotropic point (as indicated by the open circle on the figure).
21. Determine the activity coefficient of ethanol and hexane, respectively, in the liquid phase at the azeotropic point.

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22. Determine the change of Gibbs free energy in the process of mixing 0.74 mol of pure hexane and 0.26 mol of pure ethanol under constant temperature of 298 K and pressure of 0.241 bar.

The following mechanism is proposed for a catalytic reaction A→ R:

$A + E \underset{k_2}{\overset{k_1}{\rightleftarrows}} X$

$X \xrightarrow{k_3} R + E$

and E is the catal yst with $[E_0]=[E]+[X]$, where [Y] is the concentration of species Y (Y represents A, E, X, or R) and $[E_0]$ is the initial [E].

23. Express the R formation rate as a function of $k_i$ (i=1~3), [A], and $[E_0]$. Also list assumptions made.
24. Show that the above mechanism can explain the fact that the rate is proportional to $[E_0]$ under low [A]
25. Show that the above mechanism can explain the switch of the reaction order in A when [A] increases from low to high values. And state the reaction order under high [A].

26. The rate constant for a 2nd order irreversible reaction at 30°C is found to be twice as the value at 20°C. What is the activation energy?

27. Consider a chain of successive first order reactions $A \rightarrow R \rightarrow S \rightarrow T$. Show that in a concentration-time plot for each species, the maximum concentration of S and the inflection point of T occur at the same time.

For the following cell at 25 °C: Pt, $H_2$(1bar) | HCl (0.01 m) | AgCl(s) | Ag:

28. Write down the reactions for each electrode and schematically plot (sketch) the cell. In the schematic plot, clearly indicate the electrode arrangement, solution, and the salt bridge, if there is any.
29. If the emf of this cell is 0.2003 V at 24 °C, 0.2002 V at 25 °C, and 0.2001 at 26°C while the pressure remains at 1 bar. What are ΔG, ΔS, and ΔH of the overall cell reaction at 25 °C? You may make extra assumptions if needed.

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