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國立臺灣大學 102 學年度碩士班招生考試試題

科目:物理化學(A)

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第一部分單選題,每題3分,請務必使用試卷第一頁[選擇題作答區]作答

- (1). Use the data given in Table 1. A substance of 4.50 g is dissolved in 125 g of CCl₄ (carbon tetrachloride) that leads to an elevation of boiling point of 0.650 K. Approximately, what is the freezing point depression?
- (a) 2 K
- (b) 1 K
- (c) -4 K(d) -8 K
- (e) -10 K

Table 1. Freezing Point Depression and Boiling Point Elevation Constants

Substance	Standard Freezing	$K_f(K \log mol^{-1})$	Standard Boiling	$K_h(K \text{ kg mol}^{-1})$
	Point (K)		Point (K)	9)=
Acetic acid	289.6	3.59	391.2	3.08
Benzene	278.6	5.12	353.3	2.53
Camphor	449	40.	482.3	5.95
Carbon disulfide	161	3.8	319.2	2.40
Carbon tetrachloride	250.3	30.	349.8	4.95
Cyclohexane	279.6	20.0	353.9	2.79
Ethanol	158 <mark>.</mark> 8	2.0	351.5	1.07
Phenol	314	7.27	455.0	3.04
Water	273.15	1.86	373.15	0.51

- (2). According to (1), please calculate the factor by which the vapor pressure of CCl4 is lowered?
- (a) 0.58
- (b) 0.68
- (c) 0.78
- (d) 0.88
- (e) 0.98
- (3). At 298.15 K, ΔG_f^o (C, graphite)=0, and ΔG_f^o (C, diamond) =2.90 k J mol⁻¹.

Therefore, graphite is more stable solid phase at the temperature at $P = P^o = 1$ bar. Given that the density of graphite and diamond are 2.25 and 3.52 kg/L, respectively, at what pressure will graphite and diamond be in equilibrium at 298.15 K?

- (a) $1.51 \times 10^9 \ bar$
- (b) $1.51 \times 10^4 \ bar$
- (c) $2.91 \times 10^6 \ bar$
- (d) $2.91 \times 10^4 \ bar$
- (e) $2.91 \times 10^3 \ bar$
- (4). The variation of the equilibrium vapor pressure with temperature for liquid and solid chlorine in the vicinity of the triple point is given by

$$\ln P_t = \frac{-2661}{T} + 22.76$$

$$\ln P_s = \frac{-3755}{T} + 26.88$$

What is the triple point temperature?

- (a) 265.5 K.
- (b) 215.5 K
- (c) 195.5 K

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- (d) 145.5 K
- (e) 65.5 K
- (5). According to (4), what is the triple point pressure?
- (a) $6.4655 \times 10^2 Pa$
- (b) $6.4655 \times 10^3 Pa$
- (c) $6.4655 \times 10^5 Pa$
- (d) $3.4112 \times 10^3 Pa$
- (e) $3.4112 \times 10^5 Pa$

第二部分複選題,每題3分(全對才給分),請務必使用試卷第一頁[選擇題作答區]作答

- (6). Which of the following value is intensive?
- (a) Pressure
- (b) Density
- (c) Electromotive force (emf)
- (d) Internal energy
- (e) Ionic strength
- (7). From the data given in Table 2, for the reaction

$$C_2H_4(g) + H_2(g) \rightleftarrows C_2H_6(g)$$

Which of the following statement is correct:

- (a) K_P at 25 °C is $3.88 \times 10^{17} \ bar^{-1}$
- (b) K_c at 25 °C (standard state: 1M) is $9.615 \times 10^{18} \ dm^3 mol^{-1}$
- (c) ΔG° at 25 °C (standard state: 1M) is $-108.348 \ k J mol^{-1}$
- (d) ΔS^o at 25 °C (standard state: 1M) is $-94.1 I K^{-1} mol^{-1}$
- (e) K_P at 100 °C is $6.13 \times 10^{12} bar^{-1}$

Table 2.

	$\Delta_f H^o$	$\Delta_f G^o$	So
	$k \ J \ mol^{-1}$	$\overline{k \ J \ mol^{-1}}$	$JK^{-1} mol^{-1}$
H ⁺ (aq)	0	0	0
$H_2(g)$	0	0	130.7
HCl(aq)	-167.2	-131.3	56.48
HCN(g)	135	125	201.7
$HNO_3(1)$	-174.1	-80.7	155.6
HNO₃(aq)	-207.4	-113.3	146.4
$H_2O(g)$	241.826	-228.6	188.8
$H_2O(1)$	-285.83	-237.2	69.95
$H_2O_2(g)$	-136.3	-105.6	232.7
$H_2O_2(I)$	-187.8	-120.4	110
$H_2S(g)$	-20.6	-33.4	205.8
$H_2SO_4(1)$	-814.0	-690.0	156.9
$H_2SO_4(aq)$	-909.3	-744.6	20.08
$CH_4(g)$	-74.6	-50.5	186.3
$C_2H_2(g)$	227.4	209.9	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	-84.0	-32.0	229.2
$C_3H_8(g)$	-103.8	-23.4	270.3
$C_4H_{10}(g)$	-125.7	-17.15	310.1
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_6(1)$	49.1	124.5	173.4
$C_6H_{12}(g)$	-123.4	31.8	298.2
$C_6H_{12}(I)$	-156.2	26.7	204.3
$C_{10}H_8(g)$	150.6	224.1	333.1

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O II (1)	70.6	001.6	
$C_{10}H_8(s)$	78.5	201.6	167.4
$CH_2O(g)$	-108.6	-102.5	218.8
CH₃OH(g)	-201.0	-162.3	239.9
CH ₃ OH(l)	-239.2	-166.6	126.8
CH ₃ CHO(1)	-166.2	-133.0	263.8

(8). One mole of an ideal gas is initially at 10 bar and 298 K. It is allowed to expand against a constant external pressure of 2 bar to a final pressure of 2 bar. During this process, the temperature of the gas falls to 253.2 K. Assuming a path of isothermal expansion to (P_0, V_0) followed by adiabatic expansion to the final state, is performed. Thermal surroundings remain at 298 K throughout.

Which of the following statement is correct:

- (a) $\Delta U = -358.3 \ J \ mol^{-1}$
- (b) $\Delta U = -558.7 \ J \ mol^{-1}$
- (c) $\Delta H = -931.2 \text{ J mol}^{-1}$ (d) $\Delta H = -731.0 \text{ J mol}^{-1}$
- (e) $\Delta S = 9.994 J K^{-1} mol^{-1}$
- (9). From the Second Law of Thermodynamics, efficiency can be defined as the following:

efficiency =
$$\frac{w}{q_h} = \frac{q_h + q_c}{q_h} = \frac{T_h - T_c}{T_h}$$
 (for a reversible process)

Which of the following statement is correct:

- (a) Maximum work of 214 J that can be obtained from 1000 J of heat supplied to a steam engine with a high temperature reservoir at 100°C if the condenser is at 20°C.
- (b) Maximum work of 307 J that can be obtained from 1000 J of heat supplied to a steam engine with a high temperature reservoir at 150°C if the condenser is at 20°C.
- (c) Theoretically, a gallon of gasoline can lift an automobile weighing 2800 lb to a height of 17,000 ft against the force of gravity, if it is assumed that the cylinder temperature is 2200 K and the exit temperature is 1200 K.
- (d) High efficiency are obtained if the ratio $\frac{T_c}{T_h}$ is large.
- (e) There are no limitations to the efficiencies of fuel cells.
- (10). Which of the following statement is correct:
- (a) Molar conductivity of a weak electrolyte falls pronouncedly with increased concentration.
- (b) Molar conductivity of a strong electrolyte falls pronouncedly with decreased concentration.
- (c) The behavior of molar conductivity of a strong electrolyte can be described by Debye Hückel Theory.
- (d) The behavior of molar conductivity of a strong electrolyte can be described using the model of the drag force between positive ions and negative ions, and also of the drag force from the surrounding solvent molecules.
- (e) According to Debye-Hückel Limiting Law, the variation of log10 γ ± with the square root of the ionic strength is linear.

第三部分非選擇題,本大題請於試卷內之[非選擇題作答區]標明題號依序作答

(11). Ammonium chloride, NH₄Cl, decomposes when it is heated.

 $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

- (a.) How many components and phases are present when the salt is heated in an otherwise empty container? (4
- (b.) Now suppose that additional ammonia is also present. How many <u>components</u> and <u>phases</u> are present? (4 points)
- (12). The reaction $CaCO_3(s) + CaO(s) \rightarrow CO_2(g)$ is a equilibrium.
- (c.) How many degrees of freedom are there when all three phases are present at equilibrium? (4 points)

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(d.) How many degrees of freedom are there when only $CaCO_3(s)$ and $CO_2(g)$ are present? (4 points)

(13). The standard emf of the cell $Pt(s)|H_2(g)|HBr(aq)|AgBr(s)|Ag(s)$ was measured over a range of temperatures, and the data were fitted to the following polynomial:

 $E^{\circ}/V = 0.07131 - 4.99 \times 10^{-4} (T/K-298) - 3.45 \times 10^{-6} (T/K-298)^{2}$

Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298K.

(6 points)

Hint:

$$E = E^o - \frac{RT}{zF} \ln \left(\frac{\dots [Y]^y [Z]^z}{[A]^a [B]^b \dots} \right)$$

(14). (5 points) The stratosphere begins at 11km above the Earth's surface. At this altitude P = 22.6kPa and $T = -56.6^{\circ}C$. What is the mean free path of N_2 at this altitude? (The collisional cross section of N_2 is $0.43 \times 10^{-18} m^2$.)

(15). (5 points) Consider the first-order decomposition of cyclobutane at 438°C at constant volume. The rate constant for the reaction is $2.48 \times 10^{-4} \, s^{-1}$. What is the half-life?

(16). (10 points) Consider the interconversion of the "boat" and "chair" conformation of cyclohexane:

The reaction is first order in each direction, with an equilibrium constant of 10^4 . The activation energy for the conversion of the chair conformer to the boat conformer is 42kJ/mol. Assuming an Arrhenius pre-exponential factor of $10^{12} s^{-1}$, what is the expected observed reaction rate constant at 298K if one were to initiate this reaction starting with only the boat conformer?

(17). (10 points) Consider the schematic reaction $A \xrightarrow{k} P$. (a) If the reaction is one-half order with respect to [A], what is the integrated rate law expression for this reaction? (b) What would be the half-life for this reaction?

(18). (10 points) Consider the following mechanism for ozone thermal decomposition:

$$O_3 \xrightarrow{k_1} O_2 + O$$

$$O_3 \leftarrow O_2 + O_3 \rightarrow O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

(a) Derive the rate law expression for the loss of O_3 .

(b) Under what conditions will the rate law expression for O_3 decomposition be first order with respect to O_3 ?

(19). (8 points) Describe the following terms. Use graphs if necessary. (State and explain the variables that are used.)

- (a) Lennard-Jones potential and its important parameters.
- (b) Stokes-Einstein Equation.
- (c) Eyring equation.
- (d) The three explosion limits for the reaction of H_{2(g)} and O_{2(g)}.
- (e) Beer-Lamber law for absorption.
- (f) Langmuir adsorption isotherm equation.
- (g) Bragg's law for x-ray diffraction.
- (h) Michaelis-Mentem mechanism for enzyme reactions.