國立台灣科技大學九十五學年度碩士班招生試題

系所組別： 高分子工程系碩士班丁組

科　　目： 物理化學

1. 共 9 大題，總分 100 分。 2. 請於答案卷內依序作答。

1. At 35°C, the density of liquid ethanol is 0.777 g/cm^3 and its vapor pressure is 100 mmHg.
   (a) Calculate the vapor pressure of ethanol in 100 atm of N_2. (5%)
   (b) If the vapor pressure were 150 mmHg, then what should be the pressure of N_2? (5%)

2. For an ideal binary gas system,
   (a) what is the mixing molar ratio for maximum ΔG_{mix}? (5%)
   (b) what is the maximum ΔG_{mix} at 100°C? (5%)

3. For a reversible reaction $A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$, the following data are obtained:

t (s)	0	10	100	∞
[A] (M)	0.15	0.142	0.102	0.086

   (a) Derive the equation describing the time dependence of the concentration [A]. (5%)
   (b) Please calculate k_f and k_r. (5%)

4. Water is vaporized reversibly at 100 degrees centigrade and 1.013 bar (1 bar= 100,000 kg/m/s/s). The heat of vaporization is 40.69 kJ/ mol.
   (a) Find the work causing this change. (3%)
   (b) What is the value of the change of internal energy? (3%)
   (c) What is the value of heat? (2%)

5. For 1.0 mol of an ideal binary solution at 25 degrees centigrade, sketch plots of
   (a) enthalpy of mixing (2%), (b) entropy of mixing (2%),
   (c) volume of mixing (2%), and (d) Gibbs energy of mixing (2%), versus the mole fraction of a component.

6. (a) Give the physical meaning of Bohr radius, a, in quantum theory. (2%)
   (b) For the 1s orbital of hydrogen atom, the wave function of an electron is F. Show the expression indicating the probability of finding the electron within the Bohr radius from the nucleus. (3%)
   (c) Show a quantitative relationship between F (wave function) and a (Bohr radius). (3%)

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7. Real gases show deviations from the ideal gas law because molecules interact with each other.
   (a) Show graphically the potential energy dependency of two molecules on their separation. (2%)
   (b) Label the molecular diameter on this plot. (3%)
   (c) What are two types of molecular interactions involved? (3%)

8. (a) Given the equilibrium internuclear distance of HCl is 0.13 nm, estimate the reduced mass and moment of inertia of the molecule. (6%)
   (Atomic mass of H= 1.008 g/mol and Cl= 34.969 g/mol)
   (b) In conjunction with the above calculation, describe the way you can determine experimentally the bond length of HCl. (2%)

9. One method for the manufacture of "synthesis gas" (primarily a mixture of CO and H_2) is the catalytic reforming of $CH_{4(g)}$ with steam at high temperature and atmospheric pressure (R1):

$$\text{R1: } CH_{4(g)} + H_2O_{(g)} = CO_{(g)} + 3H_{2(g)}$$

The only other reaction which occurs to an appreciable extent is the water-gas-shift reaction (R2):

$$\text{R2: } CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$$

If the reactants are supplied in the ratio, 2 mole steam to 1 mole CH_4, and if heat supplied to the reactor so that the products reach a temperature of 1300 K, the CH_4 is completely converted and the product stream contains 17.4 mole percent CO Assuming the reactants to be preheated to 600 K, answer following questions.

(a) Calculate the standard heat of reaction at 25℃ for these two reaction (R1 & R2).All information you need is listed in Table 1. (8%)
(b) How many moles of $CO_{(g)}$ have been produced in these synthesis process. (7%)
(c) Calculate the heat requirement for the reactor. (15%)

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Table 1 Standard heats of formation at 25°C†

Joules per mole of the substance formed

Chemical species		State	ΔH°_{298}
Paraffins:			
Methane	CH_4	g	−74,520
Ethane	C_2H_6	g	−83,820
Propane	C_3H_8	g	−104,680
n-Butane	C_4H_{10}	g	−125,790
n-Pentane	C_5H_{12}	g	−146,760
n-Hexane	C_6H_{14}	g	−166,920
n-Heptane	C_7H_{16}	g	−187,780
n-Octane	C_8H_{18}	g	−208,750
1-Alkenes:			
Ethylene	C_2H_4	g	52,510
Propylene	C_3H_6	g	19,710
1-Butene	C_4H_8	g	−540
1-Pentene	C_5H_{10}	g	−21,280
1-Hexene	C_6H_{12}	g	−41,950
1-Heptene	C_7H_{14}	g	−62,760
Miscellaneous organics:			
Acetaldehyde	C_2H_4O	g	−166,190
Acetic acid	$C_2H_4O_2$	l	−484,500
Acetylene	C_2H_2	g	227,480
Benzene	C_6H_6	g	82,930
Benzene	C_6H_6	l	49,080
1,3-Butadiene	C_4H_6	g	109,240
Cyclohexane	C_6H_{12}	g	−123,140
Cyclohexane	C_6H_{12}	l	−156,230
1,2-Ethanediol	$C_2H_6O_2$	l	−454,800
Ethanol	C_2H_6O	g	−235,100
Ethanol	C_2H_6O	l	−277,690
Ethylbenzene	C_8H_{10}	g	29,920
Ethylene oxide	C_2H_4O	g	−52,630
Formaldehyde	CH_2O	g	−108,570
Methanol	CH_4O	g	−200,660
Methanol	CH_4O	l	−238,660
Methylcyclohexane	C_7H_{14}	g	−154,770
Methylcyclohexane	C_7H_{14}	l	−190,160
Styrene	C_8H_8	g	147,360
Toluene	C_7H_8	g	50,170
Toluene	C_7H_8	l	12,180

Table 1 Standard heats of formation at 25° C (*continued*)

Chemical species		State	ΔH°_{298}
Miscellaneous inorganics:			
Ammonia	NH_3	g	−46,110
Calcium carbide	CaC_2	s	−59,800
Calcium carbonate	$CaCO_3$	s	−1,206,920
Calcium chloride	$CaCl_2$	s	−795,800
Calcium chloride	$CaCl_2\cdot 6H_2O$	s	−2,607,900
Calcium hydroxide	$Ca(OH)_2$	s	−986,090
Calcium oxide	CaO	s	−635,090
Carbon dioxide	CO_2	g	−393,509
Carbon monoxide	CO	g	−110,525
Hydrochloric acid	HCl	g	−92,307
Hydrogen cyanide	HCN	g	135,100
Hydrogen sulfide	H_2S	g	−20,630
Iron oxide	FeO	s	−272,000
Iron oxide (hematite)	Fe_2O_3	s	−824,200
Iron oxide (magnetite)	Fe_3O_4	s	−1,118,400
Iron sulfide (pyrite)	FeS_2	s	−178,200
Lithium chloride	LiCl	s	−408,610
Lithium chloride	$LiCl\cdot H_2O$	s	−712,580
Lithium chloride	$LiCl\cdot 2H_2O$	s	−1,012,650
Lithium chloride	$LiCl\cdot 3H_2O$	s	−1,311,300
Nitric acid	HNO_3	l	−174,100
Nitrogen oxides	NO	g	90,250
	NO_2	g	33,180
	N_2O	g	82,050
	N_2O_4	g	9,160
Sodium carbonate	Na_2CO_3	s	−1,130,680
Sodium carbonate	$Na_2CO_3\cdot 10H_2O$	s	−4,081,320
Sodium chloride	NaCl	s	−411,153
Sodium hydroxide	NaOH	s	−425,609
Sulfur dioxide	SO_2	g	−296,830
Sulfur trioxide	SO_3	g	−395,720
Sulfur trioxide	SO_3	l	−441,040
Sulfuric acid	H_2SO_4	l	−813,989
Water	H_2O	g	−241,818
Water	H_2O	l	−285,830

† Taken from "TRC Thermodynamic Tables—Hydrocarbons," Thermodynamics Research Center, Texas A & M Univ. System, College Station, Texas; "The NBS Tables of Chemical Thermodynamic Properties," J. Physical and Chemical Reference Data, vol. 11, supp. 2, 1982.

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Table 2 Heat capacities of gases in the ideal-gas state†

Constants for the equation $C_P^{ig}/R = A + BT + CT^2 + DT^{-2}$ T (kelvins) from 298 K to T_{max}

Chemical species		T_{max}	A	10^3B	10^6C	$10^{-5}D$
Paraffins:						
Methane	CH_4	1,500	1.702	9.081	−2.164	
Ethane	C_2H_6	1,500	1.131	19.225	−5.561	
Propane	C_3H_8	1,500	1.213	28.785	−8.824	
n-Butane	C_4H_{10}	1,500	1.935	36.915	−11.402	
iso-Butane	C_4H_{10}	1,500	1.677	37.853	−11.945	
n-Pentane	C_5H_{12}	1,500	2.464	45.351	−14.111	
n-Hexane	C_6H_{14}	1,500	3.025	53.722	−16.791	
n-Heptane	C_7H_{16}	1,500	3.570	62.127	−19.486	
n-Octane	C_8H_{18}	1,500	8.163	70.567	−22.208	
1-Alkenes:						
Ethylene	C_2H_4	1,500	1.424	14.394	−4.392	
Propylene	C_3H_6	1,500	1.637	22.706	−6.915	
1-Butene	C_4H_8	1,500	1.967	31.630	−9.873	
1-Pentene	C_5H_{10}	1,500	2.691	39.753	−12.447	
1-Hexene	C_6H_{12}	1,500	3.220	48.189	−15.157	
1-Heptene	C_7H_{14}	1,500	3.768	56.588	−17.847	
1-Octene	C_8H_{16}	1,500	4.324	64.960	−20.521	
Miscellaneous organics:						
Acetaldehyde	C_2H_4O	1,000	1.693	17.978	−6.158	
Acetylene	C_2H_2	1,500	6.132	1.952	......	−1.299
Benzene	C_6H_6	1,500	−0.206	39.064	−13.301	
1,3-Butadiene	C_4H_6	1,500	2.734	26.786	−8.882	
Cyclohexane	C_6H_{12}	1,500	−3.876	63.249	−20.928	
Ethanol	C_2H_6O	1,500	3.518	20.001	−6.002	
Ethylbenzene	C_8H_{10}	1,500	1.124	55.380	−18.476	
Ethylene oxide	C_2H_4O	1,000	−0.385	23.463	−9.296	
Formaldehyde	CH_2O	1,500	2.264	7.022	−1.877	
Methanol	CH_4O	1,500	2.211	12.216	−3.450	
Toluene	C_7H_8	1,500	0.290	47.052	−15.716	
Styrene	C_8H_8	1,500	2.050	50.192	−16.662	
Miscellaneous inorganics						
Air		2,000	3.355	0.575	......	−0.016
Ammonia	NH_3	1,800	3.578	3.020	......	−0.186
Bromine	Br_2	3,000	4.493	0.056	......	−0.154
Carbon monoxide	CO	2,500	3.376	0.557	......	−0.031
Carbon dioxide	CO_2	2,000	5.457	1.045	......	−1.157
Carbon disulfide	CS_2	1,800	6.311	0.805	......	−0.906
Chlorine	Cl_2	3,000	4.442	0.089	......	−0.344
Hydrogen	H_2	3,000	3.249	0.422	......	0.083
Hydrogen sulfide	H_2S	2,300	3.931	1.490	......	−0.232
Hydrogen chloride	HCl	2,000	3.156	0.623	......	0.151
Hydrogen cyanide	HCN	2,500	4.736	1.359	......	−0.725
Nitrogen	N_2	2,000	3.280	0.593	......	0.040
Dinitrogen oxide	N_2O	2,000	5.328	1.214	......	−0.928
Nitric oxide	NO	2,000	3.387	0.629	......	0.014
Nitrogen dioxide	NO_2	2,000	4.982	1.195	......	−0.792
Dinitrogen tetroxide	N_2O_4	2,000	11.660	2.257	......	−2.787
Oxygen	O_2	2,000	3.639	0.506	......	−0.227
Sulfur dioxide	SO_2	2,000	5.699	0.801	......	−1.015
Sulfur trioxide	SO_3	2,000	8.060	1.056	......	−2.028
Water	H_2O	2,000	3.470	1.450	......	0.121

† Selected from H. M. Spencer, *Ind. Eng. Chem.*, 40: 2152, 1948; K. K. Kelley, *U.S. Bur. Mines Bull.*, 584, 1960; L. B. Pankratz, *U.S. Bur. Mines Bull.*, 672, 1982.