Name ……………………………………………………………ID no. ………………………Seat no. ……………...

King Mongkut's University of Technology Thonburi

Midterm Examination, Second Semester (2/2008)

Course: CHE 142 Thermodynamics II

Chemical Engineering, 2nd year

(Bilingual program)

Date: 26 December 2008

Time: 9.00 – 12.00

Please follow the instructions

1. Do all problems in the book provided.
2. There are 4 questions and 5 Tables in 6 pages, including the covering page.
3. Calculator and one A4 paper are allowed in the exam.

After you have finished with the examination, raise your hand for permission to leave the examination room,

Students are not allowed to take the examination paper out of the examination room.

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This exam is evaluated by the committee of the Department of Chemical Engineering

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Acting Head of Department

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1. Questions a) to c) are all independent. (30 points)

a) Calculate the volume occupied by 30 kg of propane at 350K and 24 bar using Pitzer correlation for compressibility factor.

b) In a half of a rigid cubic tank of edge length 0.5m, liquid propane at its vapor pressure is stored. Determine the molar volume and mass of the vapor and the molar volume and mass of liquid in this tank at 320K, using Pitzer correlation for the second virial coefficient.

Given : the vapor pressure of propane is 16 bar at 320K.

c) At the same temperature (320K), calculate the molar volume and compressibility factor of propane vapor at 2 MPa, using van der Waals equation of state for real gases.

Data : For propane, M = 44.097, T_c = 369.8K , P_c = 42.48 bar, ω = 0.152, Z_c = 0.276 and V_c = 200 $cm^3.mol^{-1}$

2. Considering the fluid that obeys the van der Waals equation of state for question a) and b): (20 points)

a) Show that ΔH may be expressed as functions of T, V and P as follows:

$$\Delta H = (PV - P'V') + \left(\frac{a}{V'} - \frac{a}{V}\right) + \int_{T'}^{T} C_P dT$$

when : P' and V' are pressure and molar volume at initial state, P and V are pressure and molar volume at final state, C_P is heat capacity at constant pressure and a is constant of van der Waals (attraction parameter).

Data : You may find the following useful $\left(\frac{\partial V}{\partial T}\right)_P dP = -\left(\frac{\partial P}{\partial T}\right)_V dV$

b) For this van der Waals fluid, develop expressions for β^{-1} (β = coefficient of thermal expansion) as function of T, V, a and b, as a and b are constant of van der Waals.

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3. During the camping on the hill, you boiled water in a container at constant pressure from $10^{\circ}C$ to $95^{\circ}C$ (boiling temperature) where water began to vaporize. The vapor pressure at this boiling temperature was lower than the normal atmospheric pressure. If you forgot this boiling water and went outside the camping, all the water would become steam. How much heat (J/mol water) did you waste? However, if all of the steam could be collected and processed until it had a temperature and pressure of $110^{\circ}C$ and 1.30 bar, respectively, how much heat (J/mol vapor) did you require for this process? Explain briefly how would you know the type of the final steam (saturated or superheated) after processing?

Assumption:

1. The only available data for vapor pressure was from Lee/Kesler, Pitzer-type correlation.
2. The steam at the final condition after the processing was assumed to be an ideal vapor.
3. The residual properties could be estimated using the Generalized correlation for the second virial coefficient.
4. All the processes have no heat loss. (30 Points)

4. A) For a binary solution of species 1 and 2 that followed Gibs/Duhem at constant T and P, prove that:

$$\Delta H_{mix} + x_2 \frac{\partial \Delta H_{mix}}{\partial x_1}\bigg|_{T,P} = \bar{H}_1 - H_1$$

When ΔH_{mix} = Enthalpy of the solution – (Summation of enthalpy of each pure species x mole fraction of each species) (15 Points)

B) Explain briefly the important/meaning of $\bar{H}_1 - H_1$ (5 Points)

R = 8.314 J mol^{-1} K^{-1} = 83.14 cm^3 bar mol^{-1} K^{-1} = 8,314 cm^3 kPa mol^{-1} K^{-1}

Table C.1: Heat Capacities of Gases in the Ideal-Gas State†

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

Chemical species		T_{max}	$C_{P_{298}}^{ig}/R$	A	$10^3\ B$	$10^6\ C$	$10^{-5}\ D$
Paraffins:							
Methane	CH_4	1500	4.217	1.702	9.081	−2.164	
Ethane	C_2H_6	1500	6.369	1.131	19.225	−5.561	
Propane	C_3H_8	1500	9.011	1.213	28.785	−8.824	
n-Butane	C_4H_{10}	1500	11.928	1.935	36.915	−11.402	
iso-Butane	C_4H_{10}	1500	11.901	1.677	37.853	−11.945	
n-Pentane	C_5H_{12}	1500	14.731	2.464	45.351	−14.111	
n-Hexane	C_6H_{14}	1500	17.550	3.025	53.722	−16.791	
n-Heptane	C_7H_{16}	1500	20.361	3.570	62.127	−19.486	
n-Octane	C_8H_{18}	1500	23.174	4.108	70.567	−22.208	
1-Alkenes:							
Ethylene	C_2H_4	1500	5.325	1.424	14.394	−4.392	
Propylene	C_3H_6	1500	7.792	1.637	22.706	−6.915	
1-Butene	C_4H_8	1500	10.520	1.967	31.630	−9.873	
1-Pentene	C_5H_{10}	1500	13.437	2.691	39.753	−12.447	
1-Hexene	C_6H_{12}	1500	16.240	3.220	48.189	−15.157	
1-Heptene	C_7H_{14}	1500	19.053	3.768	56.588	−17.847	
1-Octene	C_8H_{16}	1500	21.868	4.324	64.960	−20.521	
Miscellaneous organics:							
Acetaldehyde	C_2H_4O	1000	6.506	1.693	17.978	−6.158	
Acetylene	C_2H_2	1500	5.253	6.132	1.952	......	−1.299
Benzene	C_6H_6	1500	10.259	−0.206	39.064	−13.301	
1,3-Butadiene	C_4H_6	1500	10.720	2.734	26.786	−8.882	
Cyclohexane	C_6H_{12}	1500	13.121	−3.876	63.249	−20.928	
Ethanol	C_2H_6O	1500	8.948	3.518	20.001	−6.002	
Ethylbenzene	C_8H_{10}	1500	15.993	1.124	55.380	−18.476	
Ethylene oxide	C_2H_4O	1000	5.784	−0.385	23.463	−9.296	
Formaldehyde	CH_2O	1500	4.191	2.264	7.022	−1.877	
Methanol	CH_4O	1500	5.547	2.211	12.216	−3.450	
Styrene	C_8H_8	1500	15.534	2.050	50.192	−16.662	
Toluene	C_7H_8	1500	12.922	0.290	47.052	−15.716	
Miscellaneous inorganics:							
Air		2000	3.509	3.355	0.575	......	−0.016
Ammonia	NH_3	1800	4.269	3.578	3.020	......	−0.186
Bromine	Br_2	3000	4.337	4.493	0.056	......	−0.154
Carbon monoxide	CO	2500	3.507	3.376	0.557	......	−0.031
Carbon dioxide	CO_2	2000	4.467	5.457	1.045	......	−1.157
Carbon disulfide	CS_2	1800	5.532	6.311	0.805	......	−0.906
Chlorine	Cl_2	3000	4.082	4.442	0.089	......	−0.344
Hydrogen	H_2	3000	3.468	3.249	0.422	......	0.083
Hydrogen sulfide	H_2S	2300	4.114	3.931	1.490	......	−0.232
Hydrogen chloride	HCl	2000	3.512	3.156	0.623	......	0.151
Hydrogen cyanide	HCN	2500	4.326	4.736	1.359	......	−0.725
Nitrogen	N_2	2000	3.502	3.280	0.593	......	0.040
Nitrous oxide	N_2O	2000	4.646	5.328	1.214	......	−0.928
Nitric oxide	NO	2000	3.590	3.387	0.629	......	0.014
Nitrogen dioxide	NO_2	2000	4.447	4.982	1.195	......	−0.792
Dinitrogen tetroxide	N_2O_4	2000	9.198	11.660	2.257	......	−2.787
Oxygen	O_2	2000	3.535	3.639	0.506	......	−0.227
Sulfur dioxide	SO_2	2000	4.796	5.699	0.801	......	−1.015
Sulfur trioxide	SO_3	2000	6.094	8.060	1.056	......	−2.028
Water	H_2O	2000	4.038	3.470	1.450	......	0.121

†Selected from H. M. Spencer, *Ind. Eng. Chem.*, vol. 40, pp. 2152–2154, 1948; K. K. Kelley, *U.S. Bur. Mines Bull. 584*, 1960; L. B. Pankratz, *U.S. Bur. Mines Bull. 672*, 1982.

Table B.1: Characteristic Properties of Pure Species

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c cm^3 mol^{-1}	T_n/K
Krypton	83.800	0.000	209.4	55.02	0.288	91.2	119.8
Xenon	131.30	0.000	289.7	58.40	0.286	118.0	165.0
Helium 4	4.003	−0.390	5.2	2.28	0.302	57.3	4.2
Hydrogen	2.016	−0.216	33.19	13.13	0.305	64.1	20.4
Oxygen	31.999	0.022	154.6	50.43	0.288	73.4	90.2
Nitrogen	28.014	0.038	126.2	34.00	0.289	89.2	77.3
Air†	28.851	0.035	132.2	37.45	0.289	84.8	
Chlorine	70.905	0.069	417.2	77.10	0.265	124.	239.1
Carbon monoxide	28.010	0.048	132.9	34.99	0.299	93.4	81.7
Carbon dioxide	44.010	0.224	304.2	73.83	0.274	94.0	
Carbon disulfide	76.143	0.111	552.0	79.00	0.275	160.	319.4
Hydrogen sulfide	34.082	0.094	373.5	89.63	0.284	98.5	212.8
Sulfur dioxide	64.065	0.245	430.8	78.84	0.269	122.	263.1
Sulfur trioxide	80.064	0.424	490.9	82.10	0.255	127.	317.9
Nitric oxide (NO)	30.006	0.583	180.2	64.80	0.251	58.0	121.4
Nitrous oxide (N_2O)	44.013	0.141	309.6	72.45	0.274	97.4	184.7
Hydrogen chloride	36.461	0.132	324.7	83.10	0.249	81.	188.2
Hydrogen cyanide	27.026	0.410	456.7	53.90	0.197	139.	298.9
Water	18.015	0.345	647.1	220.55	0.229	55.9	373.2
Ammonia	17.031	0.253	405.7	112.80	0.242	72.5	239.7
Nitric acid	63.013	0.714	520.0	68.90	0.231	145.	356.2
Sulfuric acid	98.080	...	924.0	64.00	0.147	177.	610.0

†Pseudoparameters for $y_{N_2} = 0.79$ and $y_{O_2} = 0.21$. See Eqs. (6.88)–(6.90).

Table C.3: Heat Capacities of Liquids†

Constants for the equation $C_P/R = A + BT + CT^2$
T from 273.15 to 373.15 K

Chemical species	$C_{P_{298}}/R$	A	$10^3\ B$	$10^6\ C$
Ammonia	9.718	22.626	−100.75	192.71
Aniline	23.070	15.819	29.03	−15.80
Benzene	16.157	−0.747	67.96	−37.78
1,3-Butadiene	14.779	22.711	−87.96	205.79
Carbon tetrachloride	15.751	21.155	−48.28	101.14
Chlorobenzene	18.240	11.278	32.86	−31.90
Chloroform	13.806	19.215	−42.89	83.01
Cyclohexane	18.737	−9.048	141.38	−161.62
Ethanol	13.444	33.866	−172.60	349.17
Ethylene oxide	10.590	21.039	−86.41	172.28
Methanol	9.798	13.431	−51.28	131.13
n-Propanol	16.921	41.653	−210.32	427.20
Sulfur trioxide	30.408	−2.930	137.08	−84.73
Toluene	18.611	15.133	6.79	16.35
Water	9.069	8.712	1.25	−0.18

†Based on correlations presented by J. W. Miller, Jr., G. R. Schorr, and C. L. Yaws. *Chem. Eng.*, vol. 83(23), p. 129, 1976.

Table E.1: Values of Z^0

$P_r =$ T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580	0.1779
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887	0.1844
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138	0.1959
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6355	0.2901
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542	0.4648

Table E.2: Values of Z^1

$P_r =$ T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.97	−0.0010	−0.0050	−0.0101	−0.0208	−0.0450	−0.0770	−0.1647	−0.0623
0.98	−0.0009	−0.0044	−0.0090	−0.0184	−0.0390	−0.0641	−0.1100	−0.0641
0.99	−0.0008	−0.0039	−0.0079	−0.0161	−0.0335	−0.0531	−0.0796	−0.0680
1.00	−0.0007	−0.0034	−0.0069	−0.0140	−0.0285	−0.0435	−0.0588	−0.0879
1.01	−0.0006	−0.0030	−0.0060	−0.0120	−0.0240	−0.0351	−0.0429	−0.0223