

**Prince of Songkla University**  
**Department of Chemical Engineering, Faculty of Engineering**

Examination paper: Midterm Exam

Semester: 2/2010

Date: December 19, 2010

Time: 13.30-16.30

Subject: 230–213 Chemical Engineering Thermodynamics

Room: S 817

**ทุจริตในการสอบ โงยขึ้นต่ำ คือ ปรับตกในรายวิชาที่ทุจริต  
และพักการเรียน 1 ภาคการศึกษา**

ข้อสอบมีทั้งหมด 4 ข้อ 12 หน้า ให้นักศึกษาดูแลตรวจสอบความเรียบร้อย เบี้ยนชื่อและรหัสบนข้อสอบทุกหน้าก่อนลงมือทำข้อสอบ

- ไม่อนุญาตให้นำหนังสือหรือเอกสารใด ๆ เข้าห้องสอบ (Close book)
- อนุญาตเฉพาะกระดาษ A4 ที่เขียนด้วยรายมือด้วยเงิน จำนวน 1 แผ่น เข้าห้องสอบได้
- อนุญาตให้นำเครื่องคำนวณและ E-dictionary เข้าห้องสอบได้
- อนุญาตให้ทำข้อสอบด้วยดินสอ (2B ขึ้นไป) ได้
- อนุญาตให้เขียนคำตอบด้านหลังกระดาษได้ กรณีกระดาษคำตอบไม่เพียงพอ
- ไม่อนุญาตให้หยิบยืมเอกสาร เครื่องคำนวณ และผู้ดูแลห้องสอบ
- ไม่อนุญาตให้นำข้อสอบออกจากห้องสอบ

**Good Luck**  
**Merry Christmas and Happy New Year 2011**

Items	Full scores	Your scores
1	15	
2	30	
3	40	
4	15	
Total	100	

ดร.สินินาฏ คงคง  
 ผู้ออกข้อสอบ

**Mathematic Models and Tables for solving the following problems****Virial Equations**

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

**Cubic Equations***Generic Equation*

$$\text{For vapor: } Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon\beta)(Z + \sigma\beta)}$$

$$\text{For liquid: } Z = \beta + (Z + \varepsilon\beta)(Z + \sigma\beta) \left( \frac{1 + \beta - Z}{q\beta} \right)$$

$$\beta = \Omega \frac{P_r}{T_r} \quad q = \frac{\Psi \alpha(T_r)}{\Omega T_r}$$

**Generalized Correlations for gases**

$$Z = Z^0 + \omega Z^1$$

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B} \frac{P_r}{T_r}, \quad \hat{B} = \frac{BP_c}{RT_c}, \quad \hat{B} = B^0 + \omega B^1$$

$$\Rightarrow Z = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r}; \quad B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

**Generalized Correlations for liquids**

$$V^{sat} = V_c Z_c^{(1-T_r)^{2/7}} \quad \text{Raett Equation}$$

$$Z^{sat} = \frac{P_r}{T_r} Z_c^{[1+(1-T_r)^{2/7}]}$$

**Two Phase System**

$$\text{Phase transition from liquid to vapor: } \frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T \Delta V^{lv}}$$

$$\frac{\Delta H_n^{lv}}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}}, \quad \frac{\Delta H^{lv}}{\Delta H_n^{lv}} = \left( \frac{1 - T_r}{1 - T_{r_n}} \right)^{0.38}, \quad \Delta S^{lv} = \frac{\Delta H^{lv}}{T}$$

**Gas Mixture**

$$\omega \equiv \sum_i y_i \omega_i, \quad T_{pc} \equiv \sum_i y_i T_{ci}, \quad P_{pc} \equiv \sum_i y_i P_{ci}, \quad T_{Pr} = \frac{T}{T_{pc}}, \quad P_{Pr} = \frac{P}{P_{pc}}$$

**Residual Properties**

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P}, \quad V^R = \frac{RT}{P}(Z - 1)$$

$$\frac{G^R}{RT} = \frac{BP}{RT}, \quad \frac{H^R}{RT} = \frac{P}{R} \left( \frac{B}{T} - \frac{dB}{dT} \right), \quad \frac{S^R}{R} = -\frac{P}{R} \frac{dB}{dT}$$

$$H = H_0^{ig} + \int_{T_0}^T C_P^{ig} dT + H^R, \quad S = S_0^{ig} + \int_{T_0}^T C_P^{ig} dT - R \ln \frac{P}{P_0} + S^R$$

$$H = H_0^{ig} + \langle C_P^{ig} \rangle_H (T - T_0) + H^R, \quad S = S_0^{ig} + \langle C_P^{ig} \rangle_S \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} + S^R$$

$$\Delta H = \langle C_P^{ig} \rangle_H (T_2 - T_1) + H_2^R - H_1^R, \quad \Delta S = \langle C_P^{ig} \rangle_S \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R$$

$$\frac{\langle C_P^{ig} \rangle_H}{R} = A + BT_{am} + \frac{C}{3}(4T_{am}^2 - T_1 T_2) + \frac{D}{T_1 T_2}$$

$$\frac{\langle C_P^{ig} \rangle_S}{R} = A + BT_{lm} + T_{am} T_{lm} \left[ C + \frac{D}{(T_1 T_2)^2} \right], \quad T_{am} = \frac{T_1 + T_2}{2}, \quad T_{lm} = \frac{T_2 - T_1}{\ln(T_2/T_1)}$$

$$\frac{H^R}{RT_c} = P_r \left[ B^0 - T_r \frac{dB^0}{dT_r} + \omega \left( B^1 - T_r \frac{dB^1}{dT_r} \right) \right], \quad \frac{S^R}{R} = -P_r \left( \frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right)$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}, \quad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}}, \quad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}, \quad \frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}$$

**Table A.2: Values of the Universal Gas Constant**

$$\begin{aligned} R &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1} \\ &= 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} = 8,314 \text{ cm}^3 \text{ kPa mol}^{-1} \text{ K}^{-1} \\ &= 82.06 \text{ cm}^3 (\text{atm}) \text{ mol}^{-1} \text{ K}^{-1} = 62,356 \text{ cm}^3 (\text{torr}) \text{ mol}^{-1} \text{ K}^{-1} \end{aligned}$$

**Table 3.1: Parameter Assignments for Equations of State**

For use with Eqs. (3.49) through (3.56)

Eq. of State	$\alpha(T_r)$	$\sigma$	$\epsilon$	$\Omega$	$\Psi$	$Z_c$
vdW (1873)	1	0	0	1/8	27/64	3/8
RK (1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
SRK (1972)	$\alpha_{\text{SRK}}(T_r; \omega)^{\dagger}$	1	0	0.08664	0.42748	1/3
PR (1976)	$\alpha_{\text{PR}}(T_r; \omega)^{\ddagger}$	$1 + \sqrt{2}$	$1 - \sqrt{2}$	0.07780	0.45724	0.30740

$\dagger \alpha_{\text{SRK}}(T_r; \omega) = [1 + (0.480 + 1.574 \omega - 0.176 \omega^2)(1 - T_r^{1/2})]^2$

$\ddagger \alpha_{\text{PR}}(T_r; \omega) = [1 + (0.37464 + 1.54226 \omega - 0.26992 \omega^2)(1 - T_r^{1/2})]^2$

**Table E.1: Values of  $Z^0$** 

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
$T_r$								
0.80	0.9935	0.9669	0.9319	0.8539	0.0661	0.0985	0.1307	0.1626
0.85	0.9946	0.9725	0.9436	0.8810	0.0661	0.0983	0.1301	0.1614
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	0.1006	0.1321	0.1630
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	0.1359	0.1664
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	0.1410	0.1705
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  $Z^1$** 

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
$T_r$								
0.80	-0.0044	-0.0228	-0.0487	-0.1160	-0.0272	-0.0401	-0.0526	-0.0648
0.85	-0.0029	-0.0152	-0.0319	-0.0715	-0.0268	-0.0391	-0.0509	-0.0622
0.90	-0.0019	-0.0099	-0.0205	-0.0442	-0.1118	-0.0396	-0.0503	-0.0604
0.93	-0.0015	-0.0075	-0.0154	-0.0326	-0.0763	-0.1662	-0.0514	-0.0602
0.95	-0.0012	-0.0062	-0.0126	-0.0262	-0.0589	-0.1110	-0.0540	-0.0607
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

**Table E.5: Values of  $(H^R)^0 / RT_c$** 

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
$T_r$								
0.90	-0.012	-0.062	-0.126	-0.264	-0.596	-4.074	-4.094	-4.108
0.93	-0.011	-0.058	-0.118	-0.246	-0.545	-0.960	-3.920	-3.953
0.95	-0.011	-0.056	-0.113	-0.235	-0.516	-0.885	-3.763	-3.825
0.97	-0.011	-0.054	-0.109	-0.225	-0.490	-0.824	-1.356	-3.658
0.98	-0.010	-0.053	-0.107	-0.221	-0.478	-0.797	-1.273	-3.544
0.99	-0.010	-0.052	-0.105	-0.216	-0.466	-0.773	-1.206	-3.376
1.00	-0.010	-0.051	-0.103	-0.212	-0.455	-0.750	-1.151	-2.584

**Table E.6: Values of  $(H^R)^1 / RT_c$** 

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
$T_r$								
0.90	-0.014	-0.070	-0.144	-0.308	-0.751	-4.254	-4.248	-4.249
0.93	-0.012	-0.061	-0.126	-0.265	-0.612	-1.236	-3.942	-3.934
0.95	-0.011	-0.056	-0.115	-0.241	-0.542	-0.994	-3.737	-3.712
0.97	-0.010	-0.052	-0.105	-0.219	-0.483	-0.837	-1.616	-3.470
0.98	-0.010	-0.050	-0.101	-0.209	-0.457	-0.776	-1.324	-3.332
0.99	-0.009	-0.048	-0.097	-0.200	-0.433	-0.722	-1.154	-3.164
1.00	-0.009	-0.046	-0.093	-0.191	-0.410	-0.675	-1.034	-2.471

**Table E.9: Values of  $(S^R)^0 / R$** 

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
$T_r$								
0.90	-0.009	-0.046	-0.094	-0.199	-0.463	-4.145	-3.912	-3.738
0.93	-0.008	-0.042	-0.085	-0.179	-0.408	-0.750	-3.723	-3.569
0.95	-0.008	-0.039	-0.080	-0.168	-0.377	-0.671	-3.556	-3.433
0.97	-0.007	-0.037	-0.075	-0.157	-0.350	-0.607	-1.056	-3.259
0.98	-0.007	-0.036	-0.073	-0.153	-0.337	-0.580	-0.971	-3.142
0.99	-0.007	-0.035	-0.071	-0.148	-0.326	-0.555	-0.903	-2.972
1.00	-0.007	-0.034	-0.069	-0.144	-0.315	-0.532	-0.847	-2.178

**Table E.10: Values of  $(S^R)^1 / R$** 

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
$T_r$								
0.90	-0.013	-0.068	-0.140	-0.301	-0.744	-4.269	-4.249	-4.238
0.93	-0.011	-0.058	-0.120	-0.254	-0.593	-1.219	-3.914	-3.894
0.95	-0.010	-0.053	-0.109	-0.228	-0.517	-0.961	-3.697	-3.658
0.97	-0.010	-0.048	-0.099	-0.206	-0.456	-0.797	-1.570	-3.406
0.98	-0.009	-0.046	-0.094	-0.196	-0.429	-0.734	-1.270	-3.264
0.99	-0.009	-0.044	-0.090	-0.186	-0.403	-0.680	-1.098	-3.093
1.00	-0.008	-0.042	-0.086	-0.177	-0.382	-0.632	-0.977	-2.399

1. (15 points) Determine  $V$ ,  $V^R$  and  $G^R$  for steam at 523 K and 18 bar by the truncated virial equation with a value of  $B$  from the generalized Pitzer correlation.

Given:  $T_c = 647.1$  K,  $P_c = 220.55$  bar,  $\omega = 0.345$

2. (30 points) Use the Soave/Redlich/Kwong equation to calculate the molar volumes of saturated liquid ( $V^l$ ) and saturated vapor ( $V^v$ ) for iso-butane at 396 K where  $P^{\text{sat}} = 29.19$  bar, and compare results with values found by suitable generalized correlations.

Given:  $\omega=0.181$ ,  $T_c=408.1$  K,  $P_c=36.48$  bar,  $Z_c=0.282$ ,  $V_c=262.7 \text{ cm}^3 \text{ mol}^{-1}$ ,  $T_n=261.4$  K

For iteration, starting values of  $Z_0^l = 0.1641$  and  $Z_c^l = 0.5505$

- (Reserved for problem 2) -

3. (40 points) Estimate the molar enthalpy and entropy for *iso*-butane as a saturated vapor ( $H^v$ ,  $S^v$ ) and as a saturated liquid ( $H^l$ ,  $S^l$ ) at 393 K. The enthalpy (H) and entropy (S) are set equal to zero for the ideal-gas state at 1 bar and 273.15 K. The vapor pressure of *iso*-butane at 396 K is 29.19 bar.

Given:  $\omega=0.181$ ,  $T_c=408.1$  K,  $P_c=36.48$  bar,  $Z_c=0.232$ ,  $V_c=262.7 \text{ cm}^3 \text{ mol}^{-1}$ ,  $T_n=261.4$  K

$$\frac{C_p^{ig}}{R} = 1.677 + 37.853 \times 10^{-3}T - 11.945 \times 10^{-6}T^2$$

\*Clue: You should sketch the calculation path before calculation.

4. (15 points) Estimate  $H^R$  and  $S^R$  for Benzene/cyclohexane equimolar mixture at 300 K and 12 bar by the generalized second-virial-coefficient correlation.

Given; For Benzene (1):  $\omega=0.210$ ,  $T_c=562.2$  K,  $P_c=48.98$  bar,  $Z_c=0.271$ ,  $V_c=259 \text{ cm}^3 \text{ mol}^{-1}$

For Cyclohexane (2):  $\omega=0.212$ ,  $T_c=560.4$  K,  $P_c=43.50$  bar,  $Z_c=0.272$ ,  $V_c=291 \text{ cm}^3 \text{ mol}^{-1}$