UNIVERSITY OF ABERDEEN SESSION 2015–16

EX3029

Degree Examination in EX3029 Chemical Thermodynamics

14th December 2015 09.00–12.00

PLEASE NOTE THE FOLLOWING

(i) You **must not** have in your possession any material other than that expressly permitted in the rules appropriate to this examination. Where this is permitted, such material **must not** be amended, annotated or modified in any way.

(ii) You **must not** have in your possession any material that could be determined as giving you an advantage in the examination.

(iii) You **must not** attempt to communicate with any candidate during the exam, either orally or by passing written material, or by showing material to another candidate, nor must you attempt to view another candidate's work.

(iv) You **must not** take to your examination desk any electronic devices such as mobile phones or other smart devices. The only exception to this rule is an approved calculator.

Failure to comply with the above will be regarded as cheating and may lead to disciplinary action as indicated in the Academic Quality Handbook Section 7 and particularly Appendix 7.1

Notes: ***(i) Candidates ARE permitted to use an approved calculator.***

(ii) Candidates ARE NOT permitted to use the Engineering Mathematics Handbook.

(iii) Data sheets are attached to the paper.

Candidates must attempt *all* questions, each of which carries equal (20) marks. All thermodynamic symbols have their usual meanings unless otherwise stated.

Question 1

(a) Assuming $S = S\left(P, V\right)$ and taking into consideration that,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Prove that

$$\mathrm{d}S = \frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_V \mathrm{d}P + \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P \mathrm{d}V$$

[8 marks]

(b) The liquid phase esterification of acetic acid with ethanol is given by,

$$CH_3COOH + C_2H_5OH \Longleftrightarrow CH_3COOC_2H_5 + H_2O.$$

Calculate the equilibrium mole fraction of ethyl acetate at 100°C, given that initially there were 1 mole of acetic acid and 1 mole of ethanol. The standard enthalpy and Gibbs free energy of the reaction at 25°C are -3.64 kJ.mol^{-1} and -4.65 kJ.mol^{-1}, respectively. The van't Hoff equation is given by [12 marks]

$$\frac{d}{dT}\left(\ln K\right) = -\frac{\Delta H^o_{298}}{RT^2}.$$

Question 2

(a) Show that the van der Waals equation of state (vdW EOS),

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

can be expressed as a cubic polynomial equation in Z (compressibility coefficient),

$$Z^3 - (1+B)Z^2 + AZ - AB = 0$$

with $B = bP/(RT)$ and $A = aP/(RT)^2$. [7 marks]

(b) Calculate the fugacity of gaseous CO_2 at 310 K and 1.4×10^6 Pa using the van der Waals equation of state (EOS), with $a =$ 0.3658 Pa.m^6/mol^2, $b = 4.286 \times 10^{-5}$ m^3/mol. Given, [13 marks]

$$\ln\left(\frac{f}{P}\right) = -\ln\left(1 - \frac{b}{V}\right) - \frac{a}{RTV} - \ln Z + (Z-1)\,.$$

Use the largest real root of the cubic polynomial in Z to represent the gaseous phase.

Question 3

An ideal liquid mixture of 25 mol% n-pentane (nC_5), 45 mol% n-hexane (nC_6) and 30 mol% n-heptane (nC_7), initially at 69°C and high pressure, is partially vaporised by isothermically lowering the pressure to 1.013 bar. Calculate the relative amounts of vapour and liquid in equilibrium and their compositions. [20 marks]

For this problem, use

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{RT}$$

with [P] = bar, [T] = K and $[\mathrm{B}_i]$ = J.mol^{-1} and

$$\begin{array}{lll} A_{nC_5} = 10.422 & A_{nC_6} = 10.456 & A_{nC_7} = 11.431 \\ B_{nC_5} = 26799 & B_{nC_6} = 29676 & B_{nC_7} = 35200 \end{array}$$

Question 4

(a) A process stream contains light species 1 and heavy species 2. A relatively pure liquid stream containing mostly 2 is obtained through a single-stage liquid/vapour separator. Equilibrium mole fractions are x_1 = 0.002 and y_1 = 0.950. Assuming that the modified Raoult's law applies,

$$y_i P = x_i \gamma_i P_i^{\text{sat}},$$

determine T and P for the separator. The activity coefficients for the liquid phase are given by,

$$\ln \gamma_1 = 0.93 x_2^2 \quad \text{and} \quad \ln \gamma_2 = 0.93 x_1^2,$$

and the saturated vapour pressure is given by,

$$\ln P^{\text{sat}} = A - \frac{B}{T} \quad \text{with [P] = bar and [T] = [B] = K,}$$

with $A_1 = 10.08$, $B_1 = 2572.0$, $A_2 = 11.63$ and $B_2 = 6254.0$. [13 marks]

(b) Determine the temperature and composition of the first bubble created from a saturated liquid mixture of benzene and toluene containing 45 mol% percent of benzene at 200 kPa. Benzene and toluene mixtures may be considered as ideal. Given, [7 marks]

$$\ln P^{sat} = A - \frac{B}{T + C} \quad \text{with [P] = kPa and [T] = [B] = [C] = K,}$$

and

	A	B	C
Benzene	14.1603	2948.78	-44.5633
Toluene	14.2514	3242.38	-47.1806

Question 5

The molar volume $\left(\text{in cm}^3.\text{mol}^{-1}\right)$ of a binary liquid mixture at T and P is given by:

$$V = 120x_1 + 70x_2 + (15x_1 + 8x_2)\, x_1 x_2$$

(a) Find expressions for the partial molar volumes of species 1 and 2 at T and P. [7 marks]

(b) Show that these expressions satisfy the Gibbs-Duhem equation, $\sum_i x_i d\overline{M}_i = 0$, where M is an intensive thermodynamic property. [5 marks]

(c) Plot values of V, $\overline{V}_1$ and $\overline{V}_2$ calculated by the given equation for V and by the equations developed in (a) *vs* x_1. Label points $\overline{V}_1^{\infty}$ and $\overline{V}_2^{\infty}$ and show their values. [8 marks]

END OF PAPER

List of Equations

- Generic cubic equation of state:

$$Z = 1 + \beta - q\beta \frac{Z-\beta}{(Z+\varepsilon\beta)(Z+\sigma\beta)} \quad \text{(vapour and vapour-like roots)}$$

$$Z = 1 + \beta + (Z+\epsilon\beta)(Z+\sigma\beta)\left(\frac{1+\beta-Z}{q\beta}\right) \quad \text{(liquid and liquid-like roots)}$$

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

$$\alpha_{\text{SRK}} = \left[1 + \left(0.480 + 1.574\omega - 0.176\omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2$$

$$\alpha_{\text{PR}} = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2$$

EOS	α	σ	ε	Ω	Ψ
vdW	1	0	0	1/8	27/64
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	α_{SRK}	1	0	0.08664	0.42748
PR	α_{PR}	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724

- Newton-Raphson (root-finder) method: $X_i = X_{i-1} - \frac{\mathcal{F}(X_{i-1})}{d\mathcal{F}/dX\,(X_{i-1})}$

- Fundamental thermodynamic equations:

$$dU = dQ + dW; \quad dH = dU + d(PV); \quad dA = dU - d(TS); \quad dG = dH - d(TS)$$

$$dU = TdS - PdV; \quad dH = TdS + VdP; \quad dA = -SdT - PdV; \quad dG = -SdT + VdP$$

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP; \quad dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dU = C_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV; \quad dS = C_v \frac{dT}{T} - \left(\frac{\partial P}{\partial T}\right)_V dV$$

- Polytropic Relations:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad ; TV^{\gamma-1} = \text{ const}; \; TP^{\frac{1-\gamma}{\gamma}} = \text{ const}; \; PV^{\gamma} = \text{ const}$$

- Raoult's Law:

$$y_i P = x_i P_i^{\text{sat}} \quad \text{and} \quad y_i P = x_i \gamma_i P_i^{\text{sat}} \quad \text{with } i = 1, 2, \cdots N$$

- Henry's Law:

$$x_i \mathcal{H}_i = y_i P \quad \text{with } i = 1, 2, \cdots N$$

- Antoine Equation:

$$\log_{10} P^{\star} = A - \frac{B}{T+C} \quad \text{with P}^{\star} \text{ in mm-Hg and T in } ^{\circ}\text{C}$$

- Solutions:

$$M^{\mathsf{E}} = M - \sum_{i=1}^{N} x_i M_i;\ \overline{M}_1 = M + x_2 \frac{dM}{dx_1};\ \overline{M}_2 = M - x_1 \frac{dM}{dx_1}$$

Appendix A: Physical Constants and Conversion Factors

PHYSICAL CONSTANTS

Avogadro's number, $N_A = 6.023 \times 10^{26}$ molecules/kgmole
Boltzmann's constant, $k = 1.381 \times 10^{-23}$ J/(molecule·K)
Electron charge, $e = 1.602 \times 10^{-19}$C
Electron mass, $m_e = 9.110 \times 10^{-31}$ kg
Faraday's constant, F = 96,487 kC/kgmole electrons = 96,487 kJ/(V·kgmole electrons)
Gravitational acceleration (standard), $g = 32.174$ ft/s^2 = 9.807 m/s^2
Gravitational constant, $k_G = 6.67 \times 10^{-11}$m^3/(kg·s^2)
Newton's second law constant, $g_c = 32.174$ lbm·ft/(lbf·s^2) = 1.0 kg·m/(N·s^2)
Planck's constant, $\hbar = 6.626 \times 10^{-34}$ J·s/molecule
Stefan-Boltzmann constant, $\sigma = 0.1714 \times 10^{-8}$ Btu/(h·ft^2·R^4) = 5.670×10^{-8} W/(m^2·k^4)
Universal gas constant $\mathfrak{R}$ = 1545.35 ft·lbf/(lbmole·R) = 8314.3 J/(kgmole·K)
= 8.3143 kJ/(kgmole·K) = 1.9858 Btu/(lbmole·R)
= 1.9858 kcal/(kgmole·K) = 1.9858 cal/(gmole·K)
= 0.08314 bar·m^3/(kgmole·K) = 82.05 L·atm/(kgmole·K)
Velocity of light in a vacuum, $c = 9.836 \times 10^8$ ft/s = 2.998×10^8 m/s

UNIT DEFINITIONS

1 coulomb (C) = 1 A·s	1 ohm (Ω) = 1 V/A
1 dyne = 1 g·cm/s^2	1 pascal (Pa) = 1 N/m^2
1 erg = 1 dyne·cm	1 poundal = 1 lbm·ft/s^2
1 farad (F) = 1 C/V	1 siemens (S) = 1 A/V
1 henry (H) = 1 Wb/A	1 slug = 1 lbf·s^2/ft
1 hertz (Hz) = 1 cycle/s	1 tesla (T) = 1 Wb/m^2
1 joule (J) = 1 N·m	1 volt (V) = 1 W/A
1 lumen = 1 candela·steradian	1 watt (W) = 1 J/s
1 lux = 1 lumen/m^2	1 weber (Wb) = 1 V·s
1 newton (N) = 1 kg·m/s^2	

CONVERSION FACTORS

Length	Energy
1 m = 3.2808 ft = 39.37 in = 10^2 cm = 10^{10} Å	1 J = 1 N·m = 1 kg·m^2/s^2 = 9.479 × 10^{-4} Btu
1 cm = 0.0328 ft = 0.394 in = 10^{-2} m = 10^8 Å	1 kJ = 1000 J = 0.9479 Btu = 238.9 cal
1 mm = 10^{-3} m = 10^{-1}cm	1 Btu = 1055.0 J = 1.055 kJ = 778.16 ft·lbf = 252 cal
1 km = 1000 m = 0.6215 miles = 3281 ft	1 cal = 4.186 J = 3.968 × 10^{-3} Btu
1 in = 2.540 cm = 0.0254 m	1 Cal (in food value) = 1 kcal = 4186 J = 3.968 Btu
1 ft = 12 in = 0.3048 m	1 erg = 1 dyne·cm = 1 g·cm^2/s^2 = 10^{-7}J
1 mile = 5280 ft = 1609.36 m = 1.609 km	1 eV = 1.602 × 10^{-19}J

(Continued)

CONVERSION FACTORS (*Continued*)

Area

$1\ m^2 = 10^4 cm^2 = 10.76\ ft^2 = 1550\ in^2$

$1\ ft^2 = 144\ in^2 = 0.0929\ m^2 = 929.05\ cm^2$

$1\ cm^2 = 10^{-4}\ m^2 = 1.0764 \times 10^{-3}\ ft^2 = 0.155\ in^2$

$1\ in^2 = 6.944 \times 10^{-3}\ ft^2 = 6.4516 \times 10^{-4}\ m^2 = 6.4516\ cm^2$

Volume

$1\ m^3 = 35.313\ ft^3 = 6.1023 \times 10^4\ in^3 = 1000\ L = 264.171\ gal$

$1\ L = 10^{-3} m^3 = 0.0353\ ft^3 = 61.03\ in^3 = 0.2642\ gal$

$1\ gal = 231\ in^3 = 0.13368\ ft^3 = 3.785 \times 10^{-3}\ m^3$

$1\ ft^3 = 1728\ in^3 = 28.3168\ L = 0.02832\ m^3 = 7.4805\ gal$

$1\ in^3 = 16.387\ cm^3 = 1.6387 \times 10^{-5}\ m^3 = 4.329 \times 10^{-3}\ gal$

Mass

1 kg = 1000 g = 2.2046 lbm = 0.0685 slug

$1\ lbm = 453.6\ g = 0.4536\ kg = 3.108 \times 10^{-2}\ slug$

$1\ slug = 32.174\ lbm = 1.459 \times 10^4\ g = 14.594\ kg$

Force

$1\ N = 10^5\ dyne = 1\ kg \cdot m/s^2 = 0.225\ lbf$

1 lbf = 4.448 N = 32.174 poundals

$1\ poundal = 0.138\ N = 3.108 \times 10^{-2}\ lbf$

Power

$1\ W = 1\ J/s = 1\ kg \cdot m^2/s^3 = 3.412\ Btu/h = 1.3405 \times 10^{-3}\ hp$

$1\ kW = 1000\ W = 3412\ Btu/h = 737.3\ ft \cdot lbf/s = 1.3405\ hp$

$1\ Btu/h = 0.293\ W = 0.2161\ ft \cdot lbf/s = 3.9293 \times 10^{-4}\ hp$

$1\ hp = 550\ ft \cdot lbf/s = 33000\ ft \cdot lbf/min = 2545\ Btu/h = 746\ W$

Pressure

$1\ Pa = 1\ N/m^2 = 1\ kg/(m \cdot s^2) = 1.4504 \times 10^{-4}\ lbf/in^2$

$1\ lbf/in^2 = 6894.76\ Pa = 0.068\ atm = 2.036\ in\ Hg$

$1\ atm = 14.696\ lbf/in^2 = 1.01325 \times 10^5\ Pa$
$= 101.325\ kPa = 760\ mm\ Hg$

$1\ bar = 10^5\ Pa = 0.987\ atm = 14.504\ lbf/in^2$

$1\ dyne/cm^2 = 0.1\ Pa = 10^{-6}\ bar = 145.04 \times 10^{-7}\ lbf/in^2$

$1\ in\ Hg = 3376.8\ Pa = 0.491\ lbf/in^2$

$1\ in\ H_2O = 248.8\ Pa = 0.0361\ lbf/in^2$

MISCELLANEOUS UNIT CONVERSIONS

Specific Heat Units

$1\ Btu/(lbm \cdot °F) = 1\ Btu/(lbm \cdot R)$

$1\ kJ/(kg \cdot K) = 0.23884\ Btu/(lbm \cdot R) = 185.8\ ft \cdot lbf/(lbm \cdot R)$

$1\ Btu/(lbm \cdot R) = 778.16\ ft \cdot lbf/(lbm \cdot R) = 4.186\ kJ/(kg \cdot K)$

Energy Density Units

$1\ kJ/kg = 1000\ m^2/s^2 = 0.4299\ Btu/lbm$

$1\ Btu/lbm = 2.326\ kJ/kg = 2326\ m^2/s^2$

Energy Flux

$1\ W/m^2 = 0.317\ Btu/(h \cdot ft^2)$

$1\ Btu/(h \cdot ft^2) = 3.154\ W/m^2$

Heat Transfer Coefficient

$1\ W/(m^2 \cdot K) = 0.1761\ Btu/(h \cdot ft^2 \cdot R)$

$1\ Btu/(h \cdot ft^2 \cdot R) = 5.679\ W/(m^2 \cdot K)$

Thermal Conductivity

$1\ W/(m \cdot K) = 0.5778\ Btu/(h \cdot ft \cdot R)$

$1\ Btu/(h \cdot ft \cdot R) = 1.731\ W/(m \cdot K)$

Temperature

$T(°F) = \frac{9}{5} T(°C) + 32 = T(R) - 459.67$

$T(°C) = \frac{5}{9} [T(°F) - 32] = T(K) - 273.15$

$T(R) = \frac{9}{5} T(K) = (1.8) T(K) = T(°F) + 459.67$

$T(K) = \frac{5}{9} T(R) = T(R)/1.8 = T(°C) + 273.15$

Density

$1\ lbm/ft^3 = 16.0187\ kg/m^3$

$1\ kg/m^3 = 0.062427\ lbm/ft^3 = 10^{-3}\ g/cm^3$

$1\ g/cm^3 = 1\ kg/L = 62.4\ lbm/ft^3 = 10^3\ kg/m^3$

Viscosity

$1\ Pa \cdot s = 1\ N \cdot s/m^2 = 1\ kg/(m \cdot s) = 10\ poise$

$1\ poise = 1\ dyne \cdot s/cm^2 = 1\ g/(cm \cdot s) = 0.1\ Pa \cdot s$

$1\ poise = 2.09 \times 10^{-3}\ lbf \cdot s/ft^2 = 6.72 \times 10^{-2}\ lbm/(ft \cdot s)$

$1\ centipoise = 0.01\ poise = 10^{-3}\ Pa \cdot s$

$1\ lbf \cdot s/ft^2 = 1\ slug/(ft \cdot s) = 47.9\ Pa \cdot s = 479\ poise$

$1\ stoke = 1\ cm^2/s = 10^{-4}\ m^2/s = 1.076 \times 10^{-3}\ ft^2/s$

$1\ centistoke = 0.01\ stoke = 10^{-6}\ m^2/s = 1.076 \times 10^{-5}\ ft^2/s$

$1\ m^2/s = 10^4\ stoke = 10^6\ centistoke = 10.76\ ft^2/s$