UNIVERSITY OF JOHANNESBURG

PROGRAM	:	BACHELOR OF ENGINEERING TECHNOLOGY *CHEMICAL ENGINEERING*
SUBJECT	:	**CHEMICAL THERMODYNAMICS 2A**
CODE	:	**CTDCHA2**
DATE	:	WINTER EXAMINATION 1 JUNE 2019
DURATION	:	(SESSION 1) 08:30 - 11:30
WEIGHT	:	40 : 60
TOTAL MARKS	:	100

EXAMINER(S)	:	MRS N SEEDAT
MODERATOR	:	DR R HUBERTS
NUMBER OF PAGES	:	8 PAGES

REQUIREMENTS	:	Use of scientific (non-programmable) calculator is permitted (only one per candidate); graph paper

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HINTS AND INSTRUCTIONS TO CANDIDATE(S):

- Purpose of assessment is to determine not only if you can write down an answer, but also to assess whether you understand the concepts, principles and expressions involved. Set out solutions in a logical and concise manner with justification (assumptions) for the steps followed.
- **ATTEMPT ALL QUESTIONS**. Please answer each question to the best of your ability.
- Write your details (module name and code, ID number, student number etc.) on script(s).
- Number each question clearly; questions may be answered in any order.
- Make sure that you read each question carefully before attempting to answer the question.
- Show all steps (and units) in calculations; this is a 'closed book' test.
- Ensure your responses are legible, clear and include relevant units (where appropriate).
- Answers must be to FOUR significant figures.
- Hand in Graph paper with your answer paper.

Question One [Total: 31 Marks]

A reciprocating compressor initially contains air in the piston-cylinder at 0.08 m^3, 0.9 bar, and 62°C. The air is reversibly compressed to a final volume of 0.025 m^3 according to the equation $PV^{1.5}$ = constant. Take the molar mass of air as 29 g/mol, and a C_v value for air of 0.736 kJ/kg K.

1.1 State all assumptions made to solve Questions 1.2-1.6. **[2]**
1.2 Determine the mass of air in kg. **[6]**
1.3 Determine the final temperature in K. **[8]**
1.4 Determine the internal energy change in kJ. **[3]**
1.5 Determine the work required in kJ. **[7]**
1.6 Determine the magnitude and direction of any heat transfer in kJ and state if heat is added or removed from the system. **[3]**
1.7 Determine the effect on Q and W if the process was only 80% efficient. **[2]**

Question Two [Total: 18 Marks]

An irreversible heat pump is designed to remove heat from the atmosphere at 7°C and to supply 43 200 kJ/hr of heat to a constant temperature reservoir at 420 K. The efficiency of the heat pump is 80% of that of a Carnot heat pump operating between the same temperatures. The heat pump is driven, through a transmission, by the output of a heat engine which takes heat from a constant temperature reservoir at 1 050 K and rejects waste heat to the same 420 K of that of a Carnot heat engine operating between the same temperatures. In addition, the transmission which delivers the actual work output of the heat engine to the heat pump is only 75% efficient.

2.1 Draw a block diagram to depict the process. **[3]**
2.2 Determine the power input required for the actual heat pump in kW. **[6]**
2.3 Determine the rate of heat input from 1050 K reservoir to the actual engine in kJ/hr. **[5]**
2.4 Determine the percentage of the total heat supplied to the 420 K reservoir which is delivered by the heat pump. **[4]**

Question Three **[Total: 13 Marks]**

It is required to design a process in which acetone is used as a solvent. As part of your safety analysis, you need to ensure that acetone will not boil at process conditions. Apply the Antoine equation. All data required can be found in the appendices.

3.1 Determine the vapour pressure at a temperature at 100°C. **[6]**

3.2 Determine the normal boiling point. **[5]**

3.3 Can acetone be used as a solvent at the operating conditions of 100°C. **[2]**

Question Four **[Total: 22 Marks]**

Chlorine is produced by the reaction:

$4HCl_{(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)} + 2Cl_{2(g)}$

The feed stream consists of 80 mol% - HCl and 20 mol% - O_2, and it enters the reactor at 120°C. If the conversion of HCl is 100% and the products leaves the reactor at 500°C.

4.1 Determine how much heat must be transferred from the reactor per mol of the entering gas mixture. **[20]**

4.2 Which contains more chemical energy, 1 kmol of HCl or 1 kmol of H_2O? **[2]**

Data required:

$H^{\circ}_{f\ 298(HCl)}$= -92 311 kJ/mol

$H^{\circ}_{f\ 298(H2O)}$= -241 818 kJ/mol

Component	A	B	C	D
HCl	3.156	0.623×10^{-3}	0	0.151×10^{5}
O_2	3.639	0.506×10^{-3}	0	-0.227×10^{5}
H_2O	3.470	1.4550×10^{-3}	0	0.121×10^{5}
Cl_2	4.442	0.089×10^{-3}	0	-0.344×10^{5}

$C_P=A+BT+CT^2+DT^3$ with T in K and C_P in J/mol K

Question Five **[Total: 16 Marks]**

The behaviour of gases can correctly be predicted using equations of state. The molar volume of a gas can be determined empirically directly from the equation of state or can be determined from a graphical plot of the equation of state. The behaviour of n-pentane can be describes using the Peng- Robinson equation of state provided below:

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$$

The Peng-Robinson parameters for n-pentane at 100°C are:

$a = 2.417 \times 10^{12}$ Pa.cm^6/mol^2 and $b = 90.18$ cm^3/mol

5.1 Determine the pressure of n-pentane at 100°C and 100 cm^3/mol using the Peng-Robinson equation state. **[4]**

5.2 Hence or otherwise plot the pressure as a function of molar volume at a temperature of 100°C using the Peng-Robinson equation state (use volume points of 475, 480, 30 00, 30 200, 30 400 cm^3/mol). **[10]**

5.3 Using the plot generated in Question 5.2, determine the molar volume at 0.095 MPa. **[2]**

END **[Total: 100 Marks]**

APPENDIX A

USEFUL EQUATIONS AND FORMULAE

$PV = nRT$; $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; $v = \frac{V^t}{m}$; $\dot{m} = uA\rho$; $\dot{n} = \frac{uA}{vM}$;$\rho = v^{-1}$; $\dot{V} = \frac{V}{t}$

t(°C) = T(K) – 273.15; t(°F) = T(R) – 459.67; t(°F) = 1.8t(°C) + 32;

$P_g = \frac{F}{A} = \frac{mg}{A} = \frac{\rho V g}{A} = \frac{Ah\rho g}{A}$; $P_{abs} = P_g(or\ \rho gh) + P_{atm}$

Interpolation: $M = \left(\frac{X_2 - X}{X_2 - X_1}\right) M_1 + \left(\frac{X - X_1}{X_2 - X_1}\right) M_2$ OR $M = \frac{M_1(X_2 - X) + M_2(X - X_1)}{X_2 - X_1}$

Double Interpolation:

	X_1	X	X_2
Y_1	$M_{1,1}$		$M_{1,2}$
Y		$M = ?$	
Y_2	$M_{2,1}$		$M_{2,2}$

$$M = \left[\left(\frac{X_2 - X}{X_2 - X_1}\right) M_{1,1} + \left(\frac{X - X_1}{X_2 - X_1}\right) M_{1,2}\right] \frac{Y_2 - Y}{Y_2 - Y_1} + \left[\left(\frac{X_2 - X}{X_2 - X_1}\right) M_{2,1} + \left(\frac{X - X_1}{X_2 - X_1}\right) M_{2,2}\right] \frac{Y - Y_1}{Y_2 - Y_1}$$

$\Delta E_{univ} = \Delta E_{syst} + \Delta E_{surr} = 0$; $\eta = \frac{W_{irreversible}}{W_{reversible}}$; $\frac{dm_{cv}}{dt} = \Delta m = \dot{m}_{out} - \dot{m}_{in}$

Energy balance for open systems: $\frac{d(mU)_{cv}}{dt} = -\dot{m}\Delta\left[U + \frac{1}{2}u^2 + gh\right] + \dot{Q} + \dot{W}$

Energy balance for steady-state flow processes: $\Delta\dot{m}\left(H + \frac{1}{2}u^2 + gh\right) = \dot{Q} + \dot{W}_s$

Single Phase: $\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$

Mechanically reversible closed system processes:

Constant V: $Q = n\Delta U = n\int_{T_1}^{T_2} C_v dT = nC_v\Delta T$

Constant P: $Q = n\Delta H = n\int_{T_1}^{T_2} C_p dT = nC_p\Delta T$; $W = -R(T_2 - T_1)$

Constant T: $Q = -W = RT_1\ln\frac{V_2}{V_1} = -RT_1\ln\frac{P_2}{P_1} = P_1V_1\ln\frac{V_2}{V_1} = -P_1V_1\ln\frac{P_2}{P_1}$

Adiabatic: $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$; $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P}$; $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{C_P/C_V}$; $\gamma = \frac{C_P}{C_V}$;

Adiabatic: $W = \Delta U = C_V\Delta T = \frac{R\Delta T}{\gamma - 1} = \frac{R(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\gamma - 1/\gamma} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\gamma - 1/\gamma} - 1\right]$

Virial equation truncated to 2 terms: $Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$; truncated to 3 terms: $Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2}$;

Lee/ Kesler correlation: $Z = Z^o + \omega Z^1$;

Generalized Pitzer correlation: $Z = 1 + (B^0 + \omega B^1)\frac{P_r}{T_r}$; $B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$; $B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$

IG: $Q = n\Delta H = n\int_{T_0}^{T_1}\frac{Cp^{ig}}{R}dT = n\left[AT_o(\tau-1)+\frac{B}{2}T_o^2(\tau^2-1)+\frac{C}{3}T_o^3(\tau^3-1)+\frac{D}{T_o}\left(\frac{\tau-1}{\tau}\right)\right] = n\frac{\langle C_P\rangle_H}{R}(T_1 - T_0)$; where, $\tau = \frac{T}{T_0}$

$$\langle C_P\rangle_H = R\left[A+\frac{B}{2}T_o(\tau+1)+\frac{C}{3}T_o^2(\tau^2+\tau+1)+\frac{D}{\tau T_o^2}\right]$$

Clapeyron equation: $\Delta H = T\Delta V\frac{dP^{sat}}{dT}$

General entropy change: $\Delta S = C_p\ln\frac{T_2}{T_1} - ln\frac{P_2}{P_1}$

Entropy change for IG: $\frac{\Delta S}{R} = \frac{\langle C_p^{ig}\rangle_S}{R}\ln\frac{T}{T_o} - \ln\frac{P}{P_o}$; $\frac{\langle C_p^{ig}\rangle_S}{R} = A + \left[BT_o + \left(CT_o^2 + \frac{D}{\tau^2 T_o^2}\right)\left(\frac{\tau+1}{\tau}\right)\right]\left(\frac{\tau-1}{\ln\tau}\right)$

For residual properties: $V^R = V - V^{ig}$; $H^R = H - H^{ig}$; $G^R = RT\ln\phi$

$S^R = S - (S^{ig} + \frac{R}{Mr}\ln\frac{P_2}{P_1})$; $\frac{H^R}{RT_c} = \left(\frac{H^R}{RT_c}\right)^0 + \omega\left(\frac{H^R}{RT_c}\right)^1$; $\frac{S^R}{R} = \left(\frac{S^R}{R}\right)^0 + \omega\left(\frac{S^R}{R}\right)^1$

$\frac{H^R}{RT_c} = P_r\left[\left(0.083 - \frac{1.097}{T_r^{1.6}}\right) + \omega\left(0.139 - \frac{0.894}{T_r^{4.2}}\right)\right]$; $\frac{S^R}{R} = -P_r\left[\frac{0.675}{T_r^{2.6}} + \omega\left(\frac{0.722}{T_r^{5.2}}\right)\right]$;

$$Z = 1 + \beta - q\beta\frac{(Z-\beta)}{(Z+\epsilon\beta)(Z+\sigma\beta)}$$

Fugacity and fugacity coefficient: $\phi = (\phi^0)(\phi^1)^\omega$; $f = \phi P$; $\ln\phi = \sum_i X_i \ln\phi_i$; $ln\,\phi = \frac{P_r}{T_r}(B^0 + \omega B^1)$

Raoult's law: $y_iP = x_iP_i^{sat}$ where $P = \sum_i x_iP_i^{sat}$ or $P = \frac{1}{\sum_i y_i/P_i^{sat}}$

Modified Raoult's law: $y_iP = x_i\gamma_iP_i^{sat}$ where $P = \sum_i x_i\gamma_iP_i^{sat}$ or $P = \frac{1}{\sum_i y_i/\gamma_iP_i^{sat}}$

Table A.1: Conversion Factors

Quantity	Conversion
Length	1 m = 100 cm = 3.28084(ft) = 39.3701(in)
Mass	1 kg = 10^3 g = 2.20462(lb_m)
Force	1 N = 1 kg m s^{-2} = 10^5(dyne) = 0.224809(lb_f)
Pressure	1 bar = 10^5 kg m^{-1} s^{-2} = 10^5 N m^{-2} = 10^5 Pa = 10^2 kPa = 10^6(dyne) cm^{-2} = 0.986923(atm) = 14.5038(psia) = 750.061(torr)
Volume	1 m^3 = 10^6 cm^3 = 10^3 liters = 35.3147$(ft)^3$ = 264.172(gal)
Density	1 g cm^{-3} = 10^3 kg m^{-3} = 62.4278(lb_m)$(ft)^{-3}$
Energy	1 J = 1 kg m^2 s^{-2} = 1 N m = 1 m^3 Pa = 10^{-5} m^3 bar = 10 cm^3 bar = 9.86923 cm^3(atm) = 10^7(dyne) cm = 10^7(erg) = 0.239006(cal) = 5.12197 × $10^{-3}$$(ft)^3$(psia) = 0.737562(ft)($lb_f$) = 9.47831 × 10^{-4}(Btu) = 2.77778 × 10^{-7} kWhr
Power	1 kW = 10^3 W = 10^3 kg m^2 s^{-3} = 10^3 J s^{-1} = 239.006(cal) s^{-1} = 737.562(ft)(lb_f) s^{-1} = 0.947831(Btu) s^{-1} = 1.34102(hp)

Table A.2: Values of the Universal Gas Constant

R = 8.314 J mol^{-1} K^{-1} = 8.314 m^3 Pa mol^{-1} K^{-1}
= 83.14 cm^3 bar mol^{-1} K^{-1} = 8,314 cm^3 kPa mol^{-1} K^{-1}
= 82.06 cm^3(atm) mol^{-1} K^{-1} = 62,356 cm^3(torr) mol^{-1} K^{-1}
= 1.987(cal) mol^{-1} K^{-1} = 1.986(Btu)(lb mole)$^{-1}$(R)$^{-1}$
= 0.7302$(ft)^3$(atm)(lb mol)$^{-1}$(R)$^{-1}$ = 10.73$(ft)^3$(psia)(lb mol)$^{-1}$(R)$^{-1}$
= 1,545(ft)(lb_f)(lb mol)$^{-1}$(R)$^{-1}$

APPENDIX B

The constants in the table below are used to model the relationship between vapor pressure and temperature, through

$$\log_{10} P^{sat} = A - \frac{B}{T + C}$$

where P^{sat} is expressed in mm Hg and T is expressed in degrees Celsius. Note that 1 mm Hg = 133.3 Pa = 0.1333 kPa.

Name	Structure	*A*	*B*	*C*	*T* Range
Acetic acid	CH_3COOH	7.38782	1533.313	22.309	Liquid
Acetone	$(CH_3)_2CO$	7.11714	1210.595	229.664	Liquid
Acetonitrile	CH_3CN	7.11988	1314.4	230	Liquid
Acetylene	C_2H_2	9.1402	1232.6	280.9	−130 to −83
		7.0999	711.0	253.4	−82 to −72
Benzene	C_6H_6	9.1064	1885.9	244.2	−12 to 3
		6.90565	1211.033	220.790	8 to 103
Benzyl alcohol	$C_6H_5CH_2OH$	7.19817	1632.593	172.790	122 to 205
Biphenyl	$(C_6H_5)_2$	7.24541	1998.725	202.733	69 to 271
Bromochloromethane	CH_2BrCl	6.49606	942.267	192.587	16 to 68
1,3-Butadiene	C_4H_6	7.03555	998.106	245.233	−80 to −62
		6.84999	930.546	238.854	−58 to 15
n-butane	C_4H_{10}	6.80896	935.86	238.73	−77 to 19
1-butanol	C_4H_9OH	7.47680	1362.39	178.77	15 to 131
2-butanol	C_4H_9OH	7.47431	1314.19	186.55	25 to 120
1-Butene	C_4H_8	6.79290	908.80	238.54	−82 to 13
Chloroethane	C_2H_5Cl	6.98647	1030.01	238.61	−56 to 12.2
Chloroform	$CHCl_3$	6.4934	929.44	196.03	−35 to 61
Chloromethane	CH_3Cl	7.09349	948.58	249.34	−75 to −5
Cyclohexane	C_6H_{12}	6.84130	1201.53	222.65	20 to 81
Diethyl ketone	$C_5H_{10}O$	6.85791	1216.3	204	