1. (20%)

The initial state of a quantity of monatomic ideal gas is $P = 1$ atm, $V = 1$ liter and $T = 373$ K. The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume V.   This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state.

(a) Assuming all of the changes of state are conducted reversibly, please calculate the value of V and the total work done in this cycle.   Is this work done "ON" or "BY" the gas?

(b) If the change of state, either isothermal expansion, constant pressure cooling, or compression is not reversible, would V becomes larger or smaller?

2.   (10%)

Calculate the change in enthalpy and the change in entropy when one mole of α-ZrO_2 is heated from 25°C to 1000°C.

3. (10%)

A reversible heat engine, operating in a cycle, withdraws heat from a high-temperature reservoir (the temperature of which consequently decreases), performs work w, and rejects heat into a low-temperature reservoir (the temperature of which consequently increases).   The two reservoirs are, initially, at the temperatures T_1 and T_2, and have constant heat capacities C_1 and C_2 respectively.   Calculate the final temperature of the system and the maximum amount of work which can be obtained from the engine.

4.   (15%)

Please describe the Henry's law for a binary A-B solution.   Prove that in the range of composition over which the solute B obeys Henry's law, the solvent A obeys Raoult's law.

5. (15%)

Joule and Thomson showed experimentally that when a steady stream of non-ideal gas is passed through a thermally insulated tube, in which is inserted a throttle valve, the temperature of the gas changes and the state of the gas is changed from P_1, T_1 to P_2, T_2. Show that this process is isenthalpic.

6. (15%)

You are responsible for the purchase of oxygen gas which, before use, will be stored at a pressure of 200 atm at 300 K in a cylindrical vessel of diameter 0.2 meters and height 2 meters.

Would you prefer that the gas behaves ideally or as a van der Waals gas? <u>You have to state your reasons</u>.

[The van der Waals constants for oxygen are $a = 1.36$ liters^2-atm/mole^2 and $b = 0.0318$ liter/mole.]

7. (15%)

Determine the maximum pressure of water vapor in wet hydrogen at 1 atm pressure in which chromium can be heated without oxidation occurring at 1500 K. Is the oxidation of Cr by water vapor exothermic or endothermic?

* *

Atmosphere   1 atm = 1.01325 bar = 101.325 kPa
Gas constant $R = 8.3144$ joules/degree-mole
                      $= 82.06$ cm^3-atm/degree-mole
Boltzmann's constant $k = 1.38054 \times 10^{-23}$ joules/degree

Table A-1 The standard Gibbs free energy changes for several reactions (standard states are noted by subscript)

Reaction	$\Delta G°$, joules	Range, K
$2Ag_{(s)} + \frac{1}{2}O_{2(g)} = Ag_2O_{(s)}$	$-30,540 + 66.11\,T$	298–463
$Al_{(l)} = [Al]_{(1\ wt\%\ in\ Fe)}$	$-43,100 - 32.26\,T$	
$2Al_{(l)} + 1.5O_{2(g)} = Al_2O_{3(s)}$	$-1,687,200 + 326.8\,T$	993–2327
$C_{(s)} + \frac{1}{2}O_{2(g)} = CO_{(g)}$	$-111,700 - 87.65\,T$	298–2000
$C_{(s)} + O_{2(g)} = CO_{2(g)}$	$-394,100 - 0.84\,T$	298–2000
$C_{(s)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}S_{2_0} = COS_{(g)}$	$-202,800 - 9.96\,T$	773–2000
$C_{(gr)} + 2H_{2(g)} = CH_{4(g)}$	$-91,040 + 110.7\,T$	773–2000
$C_{(gr)} = [C]_{(1\ wt\%\ in\ Fe)}$	$22,600 - 42.26\,T$	
$CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)}$	$-168,400 + 144\,T$	449–1150
$2CaO_{(s)} + SiO_{2(s)} = 2CaO \cdot SiO_{2(s)}$	$-118,800 - 11.30\,T$	298–2400
$CoO_{(s)} + SO_{3(g)} = CoSO_{4(s)}$	$-227,860 + 165.3\,T$	298–1230
$2Cr_{(s)} + 1.5O_{2(g)} = Cr_2O_{3(s)}$	$-1,110,100 + 247.3\,T$	298–1793
$2Cu_{(s)} + \frac{1}{2}O_{2(g)} = Cu_2O_{(s)}$	$-162,200 + 69.24\,T$	298–1356
$2Cu_{(l)} + \frac{1}{2}O_{2(g)} = Cu_2O_{(s)}$	$-188,300 + 88.48\,T$	1356–1509
$2Cu_{(s)} + \frac{1}{2}S_{2(g)} = Cu_2S_{(s)}$	$-131,800 + 30.79\,T$	708–1356
$3Fe_{(\alpha)} + C_{(gr)} = Fe_3C_{(s)}$	$29,040 - 28.03\,T$	298–1000
$3Fe_{(\gamma)} + C_{(gr)} = Fe_3C_{(s)}$	$11,234 - 11.00\,T$	1000–1137
$Fe_{(s)} + \frac{1}{2}O_{2(g)} = FeO_{(s)}$	$-263,700 + 64.35\,T$	298–1644
$Fe_{(l)} + \frac{1}{2}O_{2(g)} = FeO_{(l)}$	$-256,000 + 53.68\,T$	1808–2000
$3Fe_{(s)} + 2O_{2(g)} = Fe_3O_{4(s)}$	$-1,102,200 + 307.4\,T$	298–1808
$Fe_{(s)} + \frac{1}{2}S_{2(g)} = FeS_{(s)}$	$-150,200 + 52.55\,T$	412–1179
$H_{2(g)} + Cl_{2(g)} = 2HCl_{(g)}$	$-188,200 - 12.80\,T$	298–2000
$H_{2(g)} + I_{2(g)} = 2HI_{(g)}$	$-8370 - 17.65\,T$	298–2000
$H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)}$	$-247,500 + 55.85\,T$	298–2000
$Hg_{(v)} + \frac{1}{2}O_{2(g)} = HgO_{(s)}$	$-152,200 + 207.2\,T$	
$Li_{(g)} + \frac{1}{2}Br_{2(g)} = LiBr_{(g)}$	$-333,900 + 42.09\,T$	1289–2000
$Mg_{(l)} + Cl_{2(g)} = MgCl_{2(l)}$	$-603,200 + 121.43\,T$	987–1368
$Mg_{(g)} + \frac{1}{2}O_{2(g)} = MgO_{(s)}$	$-729,600 + 204\,T$	1363–2200
$2MgO_{(s)} + SiO_{2(s)} = Mg_2SiO_{4(s)}$	$-67,200 + 4.31\,T$	298–2171
$MgO_{(s)} + CO_{2(g)} = MgCO_{3(s)}$	$-117,600 + 170\,T$	298–1000
$MgO_{(s)} + Al_2O_{3(s)} = MgO \cdot Al_2O_{3(s)}$	$-35,560 - 2.09\,T$	298–1698
$Mn_{(s)} + \frac{1}{2}O_{2(g)} = MnO_{(s)}$	$-388,900 + 76.32\,T$	298–1517
$N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$	$-87,030 + 25.8\,T\ln T + 31.7\,T$	298–2000
$2Ni_{(s)} + O_{2(g)} = 2NiO_{(s)}$	$-471,200 + 172\,T$	298–1726
$2Ni_{(l)} + O_{2(g)} = 2NiO_{(2)}$	$-506,180 + 192.2\,T$	1726–2200
$\frac{1}{2}O_{2(g)} = [O]_{(1\ wt\%\ in\ Fe)}$	$-111,070 - 5.87\,T$	
$Pb_{(l)} + \frac{1}{2}O_{2(g)} = PbO_{(s)}$	$-208,700 + 91.75\,T$	600–1158
$Pb_{(l)} + \frac{1}{2}O_{2(g)} = PbO_{(l)}$	$-181,200 + 68.03\,T$	1158–1808
$Pb_{(l)} + \frac{1}{2}S_{2(g)} = PbS_{(s)}$	$-163,200 + 88.03\,T$	600–1386
$PbO_{(s)} + SO_{2(g)} + \frac{1}{2}O_{2(g)} = PbSO_{4(s)}$	$-401,200 + 261.5\,T$	298–1158
$PCl_{3(g)} + Cl_{2(g)} = PCl_{5(g)}$	$-95,600 - 7.94\,T\ln T + 235.2\,T$	298–1000

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Table A-2 The constant-pressure molar heat capacities of various substances ($c_p = a + bT + cT^{-2}$ J/mole·K)

Substance	a	$b \times 10^3$	$c \times 10^{-5}$	Range, K	Remarks
Ag	21.30	8.54	1.51	298–1234 (T_m)	
Ag$_{(l)}$	30.50	—	—	1234–1600	
Al	31.38	−16.4	−3.60	298–934 (T_m)	$+20.75 \times 10^{-6}T^2$
Al$_{(l)}$	31.76	—	—	934–1600	
Al$_2$O$_3$	117.49	10.38	−37.11	298–2325 (T_m)	
Ba$_{(\alpha)}$	−473.2	1587.0	128.2	298–648	
Ba$_{(\beta)}$	0.67	−975.7	−710.0	648–1003	$−428.4 \times 10^{-6}T^2$
BaO	50.29	7.20	−4.60	298–2286 (T_m)	
BaTiO$_3$	121.46	8.54	−19.16	298–1800	
C$_{(graphite)}$	0.11	38.94	−1.48	298–1100	$−17.38 \times 10^{-6}T^2$
C$_{(graphite)}$	24.43	0.44	−31.63	1100–4000	
C$_{(diamond)}$	9.12	13.22	−6.19	298–1200	
CO	28.41	4.10	−0.46	298–2500	
CO$_2$	44.14	9.04	−8.54	298–2500	
Ca$_{(\alpha)}$	16.02	21.51	2.55	298–716	
Ca$_{(\beta)}$	−0.45	41.35	—	716–1115	
CaO	50.42	4.18	−8.49	298–1177	
CaTiO$_3$	127.49	5.69	−27.99	298–1530	
Cr	21.76	8.98	−0.96	298–2130 (T_m)	$+2.26 \times 10^{-6}T^2$
Cr$_2$O$_3$	119.37	9.30	−15.65	298–1800	
Cu	30.29	−10.71	−3.22	298–1356 (T_m)	$+9.47 \times 10^{-6}T^2$
Fe$_{(\alpha)}$	17.5	24.8	—	298–1187	
Fe$_{(\gamma)}$	7.70	19.5	—	1187–1664	
Fe$_{(\delta)}$	43.9	—	—	1664–1809	
Fe$_{(l)}$	41.84	—	—	1809–1873	
H$_2$O$_{(g)}$	30.00	10.71	0.33	298–2500	
O$_{2(g)}$	29.96	4.18	−1.67	298–3000	
2MgO.2Al$_2$O$_3$.5SiO$_2$	626.34	91.21	−200.83	298–1738 (T_m)	
N$_2$	27.87	4.27	—	298–2500	
Si$_3$N$_4$	76.36	109.04	−6.53	298–900	$−27.07 \times 10^{-6}T^2$
SiO$_{(hi-quartz)}$	43.93	38.83	−9.69	298–847	
Ti	24.94	6.57	−1.63	298–1155	$+1.34 \times 10^{-6}T^2$
TiO$_{2(rutile)}$	73.35	3.05	−17.03	298–1800	
Zr$_{(\alpha)}$	22.84	8.95	−0.67	298–1136	
Zr$_{(\beta)}$	21.51	6.57	36.69	1136–2128	
ZrO$_{2(\alpha)}$	69.62	7.53	−14.06	298–1478	
ZrO$_{2(\beta)}$	74.48	—	—	1478–2950 (T_m)	

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TABLE A-3: THE STANDARD MOLAR HEATS OF FORMATION AND MOLAR ENTROPIES OF VARIOUS SUBSTANCES AT 298 K
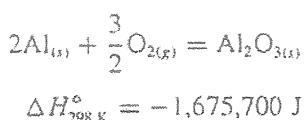
Example—For the reaction

$$2Al_{(s)} + \frac{3}{2}O_{2(g)} = Al_2O_{3(s)}$$

$$\Delta H^{\circ}_{298\,K} = -1,675,700 \text{ J}$$

Table A-3 The standard molar heats of formation and molar entropies of various substances at 298 K

Substance	ΔH°_{298}, J	S°_{298}, J/K
Al_2O_3	−1,675,700	50.9
Ba	—	62.4
BaO	−548,100	72.1
$BaTiO_3$	−1,653,100	107.9
$C_{(graphite)}$	—	5.74
$C_{(diamond)}$	1500	2.37
CH_4	−74,800	186.3
CO	−110,500	197.5
CO_2	−393,500	213.7
Ca	—	41.6
CaO	−634,900	38.1
$CaTiO_3$	−1,660,600	93.7
$3CaO.Al_2O_3.3SiO_2$	−6,646,300	241.4
$CaO.Al_2O_3.SiO_2$	−3,293,200	144.8
$CaO.Al_2O_3.2SiO_2$	−4,223,700	202.5
$2CaO.Al_2O_3.SiO_2$	−3,989,400	198.3
Cr_2O_3	−1,134,700	81.2
$H_2O_{(g)}$	−241,800	232.9
N_2	—	191.5
O_2	—	205.1
$SiO_{2\,(\alpha-quartz)}$	−910,900	41.5
Si_3N_4	−744,800	113.0
Ti	—	30.7
TiO	−543,000	34.7
Ti_2O_3	−1,521,000	77.2
Ti_3O_5	−2,459,000	129.4
TiO_2	−944,000	50.6
Zr	—	39.0
ZrO_2	−1,100,800	50.4