COLLEGE OF ENGINEERING
Department of Metallurgical & Materials Engineering
The University of Alabama

MTE 562 Thermodynamics

Quiz I

Q. 1

(10 pts) a. Explain the following: TiO_2

1. Work
2. Compressibility factor (Z)

$+2 \; +k \; -2$

(20 pts) b. Estimate the heat capacity $Cp_{,298}$ of $BaTiO_3$ using the data listed in Table - 1 and 2. The experimentally determined Cp for this compound is as follows:

$$Cp = 29.03 + (2.04 \times 10^{-3}\, T) - (4.58 \times 10^{5}\, T^{-2})\ \text{Cal/mole.K}$$

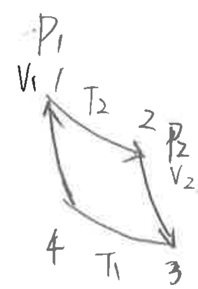
Compare the estimated value with the experimental value.

Q. 2

(5 pts) a. Define the Carnot theorem.

(10 pts) c. Express the entropy of reaction [Mg (s, 298 K) = Mg (l, T K)] of pure Magnesium, Mg, ($\Delta H_T - \Delta H_{298}$) as a function of temperature from the attached phase diagram.

(20 pts) c. A Carnot heat engine operates between reservoirs at 1200°C and 200°C. The isothermal process at the hotter reservoir consists of an expansion (reversible) from an initial pressure of 5×10^5 N/m^2 to 4×10^4 N/m^2. Assuming that the working substance is 1 kilomole of ideal gas, calculate a) the efficiency of the heat engine, b) the heat absorbed from the hotter reservoir, and c) the heat rejected to the colder reservoir.



$Q_2 + Q_1 = 0.677\,Q_2$

$dE = C_v dT = 0$

$Q = -W = pdv$

Q.3

(5 pts) a. Define the Third Law of Thermodynamics.

$PV = RT$

$PV = RT$

$P_1V_1 = P_2V_2$

$\frac{P_1}{P_2} = \frac{V_2}{V_1}$

(10 pts) b. Show that the entropy of mixing (ΔS) for one mole of ideal gas mixture is

$$\Delta S = -R\sum_{i=1}^{C} X_i \ln X_i$$

where X_i is the mole fraction of i^{th} gas and R is the gas constant.

(20 pts) c. For the reaction C(s) + 0.5 O_2 (g) = CO (g), the standard Gibbs energy change, ΔG^o, is given by

$$\Delta G^o = -111{,}710 - 87.66\,T \text{ Joules}$$

Find a) the entropy change, ΔS^o, and b) the enthalpy change, ΔH^o, for the reaction.

$\Delta G = -T\Delta S$

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89/100

Q.1

a. 1. Work is done when a force acts through a distance.

$$W = \int F\,dl = -\int p\,dV$$

5

2. Compressibility factor is used to correlate the relationships among P, V, T for real gases. It's dimensionless ~~con~~ · emperical factor. $z = \frac{PV}{RT}$

5

b. The experimental value of $C_{p,298}$ is:

$$C_{p,298} = \int_0^{298} C_p\,dT = \int_0^{298} [29.03 + (2.04\times10^{-3}\,T) - (4.58\times10^{5}\,T^{-2})]\,dT$$

$$= (29.03T + 2.04\times10^{-3}\times0.5T^2 + 4.58\times10^{5}\,T^{-1})\Big|_0^{298}$$

$$= 29.03\times298 + 2.04\times10^{-3}\times0.5\times298^2 + 4.58\times10^{5}\times\frac{1}{298}$$

$$= 8650.94 + 90.58 + 1536.91$$ check!!!

$$= 10278.43\ \text{Cal/mole}\cdot K = 43004.95\ J/\text{mole}\cdot K$$

J

17

102.4 J/mol·K

The estimated value of C_{p298}:

$BaO \cdot TiO_2$

$$(C_{p,298})_{est} = [C_{p298}(Ba) + C_{p298}(Ti) + 3C_{p298}(O)]\cdot N_A$$

$$= (27.2 + 23.8 + 3\times16.7)\times6.02\times10^{23}$$

$$= 6.0862\times10^{25}\ J/g\cdot\text{mole}\cdot K$$ too high

101.1 J/mol·K

Comparision between Cp(est.) & Cp(exp.)?

experiment value

$$C_{p,298} = 29.03 + (2.04\times10^{-3})\times298 - (4.58\times10^{5}\times298^{-2}) = 24.481\ \text{cal/mol}\cdot k = 102.43\ J/\text{mol}\cdot K$$

estimated value:

$$C_{p,298} = C_{p298}(Ba) + C_{p298}(Ti) + C_{p298}(O^{2-})^{+2} + 2C_{p298}(O^{2-})^{+4}$$

$$= 27.2 + 23.8 + 19.3 + 2\times15.9 = 102.1\ J/\text{mol}\cdot K$$

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Q.2

a. Carnot theorem: The reversibile cyclic engines operated at two fixed temperatures have the same efficiency. Efficiency $= 1 - \frac{T_1}{T_2}$

4

b. Mg: $T_{fusion} = 650°C = 923K$.

8

$$\Delta H_T - \Delta H_{298} = \int_{298}^{923} C_p(s)\, dT + H_{fusion} + \int_{923}^{T} C_p(l)\, dT$$

$$\Delta S_T = \frac{\Delta H_T - \Delta H_{298}}{T} = \int_{298}^{923} \frac{C_p(s)}{T} dT + \frac{H_{fusion}}{T} + \int_{923}^{T} \frac{C_p(l)}{T} dT$$

$S = ?$

c. a) The efficiency of the heat engine: $\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{473}{1473} = 0.679$

20

b) $Q_{iso} = -W = \int p\,dV = \int \frac{nRT_2}{V} dV = nRT_2 \ln \frac{V_2}{V_1}$

$\because$ T_2 is constant, $P_1V_1 = P_2V_2$, $V_2/V_1 = P_1/P_2$

so $Q_{iso} = nRT_2 \ln \frac{P_1}{P_2} = 1000 \times 8.31 \times 1473 \times \ln \frac{5\times10^5}{4\times10^4} = 3.09 \times 10^7$ J

c) $\eta = \frac{Q_2 + Q_1}{Q_2} = 0.679$, so $Q_1 = (0.679 - 1) Q_2 = -9.92 \times 10^6$ J

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Q3.

a. The entropy of each pure element or pure compound at their stable molecular configuration can be taken to zero at zero Kelvin.

5

b. The entropy for the ith gas is

$$\Delta S_i = -n_i R \ln \frac{V_i}{V}, \quad = -n_i R \ln X_i$$

$$V_i / V = X_i,$$

10 so $\Delta S = \sum_{i=1}^{c} \Delta S_i = \sum_{i=1}^{c} (-n_i R \ln X_i) = -R \sum_{i=1}^{c} n_i \ln X_i$

for one mole of ideal gas mixture, the mole number of the ith gas equals

$$n_i = X_i \cdot 1 = X_i,$$

so $\Delta S = -R \sum_{i=1}^{c} X_i \ln X_i$

c. a) $\Delta S^\circ = -\frac{\Delta G^\circ}{T} = \frac{+(-111710 - 87.66T)}{T} = \frac{111710}{T} + 87.66$ (J/k)

b) $\Delta H^\circ = T\Delta S^\circ = T\left(\frac{111710}{T} + 87.66\right) = 111710 + 87.66$ (J)

15

$\Delta G = -111710 - 87.66\,T$

$= \Delta H - \Delta S\,T$

$\Delta H = -111{,}710\,J$; $\Delta S = 87.66\,J/K$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = -111710 - 87.66T$ J

$\Delta H = -111710$ J

$\Delta S = 87.66$ J/k

Table 1: Atomic contributions to C_{P298}

Ag 25.5	H 6.3[b]	Pt 26.4
Al 14.6 (23.4)	Hf 26.4	Rb 26.4
As 21.3	Hg 26.4	Rh 25.9
Au 26.4	I [28.5]	S [20.9]
B 5.4 (10.9)	In 23.4	Sb 25.5
Ba 27.2	Ir 26.4	Sc 20.1
Be 7.5 (11.7)	K 25.9	Se [27.2]
Bi 27.2	La 27.2	Si 12.6 (20.1)
Br [27.6]	Lanthanides 26.4	Sn 25.5
C [8.4] [10.5][a]	Li 20.5	Sr 25.5
Ca 23.4 [25.1]	Mg 18.4 (23.8)	Ta 26.4
Cd 25.1	Mn 25.1	Te ?
Cl [25.1]	Mo 25.5	Th 28.0
Co 25.1	N 18.8 (18.8)	Ti 23.8
Cr 25.1	Na 25.1	Tl 25.5
Cs 26.8	Nb 25.9	U 28.9
Cu 25.1	Ni 25.1	V 25.1
F [22.2]	O [16.7]	W 27.2
Fe 25.5	P 15.1	Y 23.4
Ga 20.1	Pb 27.2	Zn 22.6 (25.1)
Ge 21.8	Pd 25.5	Zr 25.5

Note: Units are J/g·atom·°K. Use the values in parentheses for intermetallics, carbides, silicides, borides, and non-valence nitrides. Use the values in square brackets to estimate values not listed in Table 3−2.

[a] For saltlike carbides, such as CaC_2 and Al_4C_3, use C = 16.7.

[b] For H in acids, acid salts, and hydrides.

Special values: NH_4^+ = 57.3; H_2O = 41.0 in hydrates.

Source: Kellogg (reference 4), p. 363.

Table 2: Anion contributions to C_{P298}

	Cation charge					
Species	+1	+2	+3	+4	+5	+6
F^-	23.0	22.2	21.3	20.9	21.3	(22.6)
Cl^-	25.5	25.1	24.3	23.8		(23.8)
Br^-	27.6	27.6	27.6	26.4		
I^-	28.5	28.5	(29.3)	(28.5)		
O^{2-}	17.6	19.3	17.2	15.9	15.1	17.2
S^{2-}	29.3	23.8	23.0	20.9		
Se^{2-}	(31.4)	(27.2)				
Te^{2-}		(46.0)	(36.8)	(25.1)		
N^{3-}	(15.9)	22.2	16.7	16.7	(19.7)	
OH^-	(32.2)	29.7				
SH^-	(52.7)					
SeH^-	(46.9)					
CO_3^{2-}	60.7	57.7				
NO_3^-	69.0	62.8	(58.6)			
SO_3^{2-}	(69.9)	(68.2)				
ClO_3^-	75.7	(71.1)				
BrO_3^-	(79.1)	75.3				
IO_3^-	(79.5)					
SO_4^{2-}	79.1	76.2	74.9	(72.8)		
ClO_4^-	80.3					
CrO_4^{2-}	92.9					
$Cr_2O_7^{2-}$		107.5				
BH_4^-	64.9					
CN^-	(37.7)	(37.7)	(33.5)			

Note: The values in parentheses are based on scant evidence. The units are J/g·atom·°K.
Source: Kellogg (reference 4), p. 364.

1 g·atom = 1 mole

Ba Ti O C_p

BaO · TiO_2 +4 O

2+ 4+ 2-

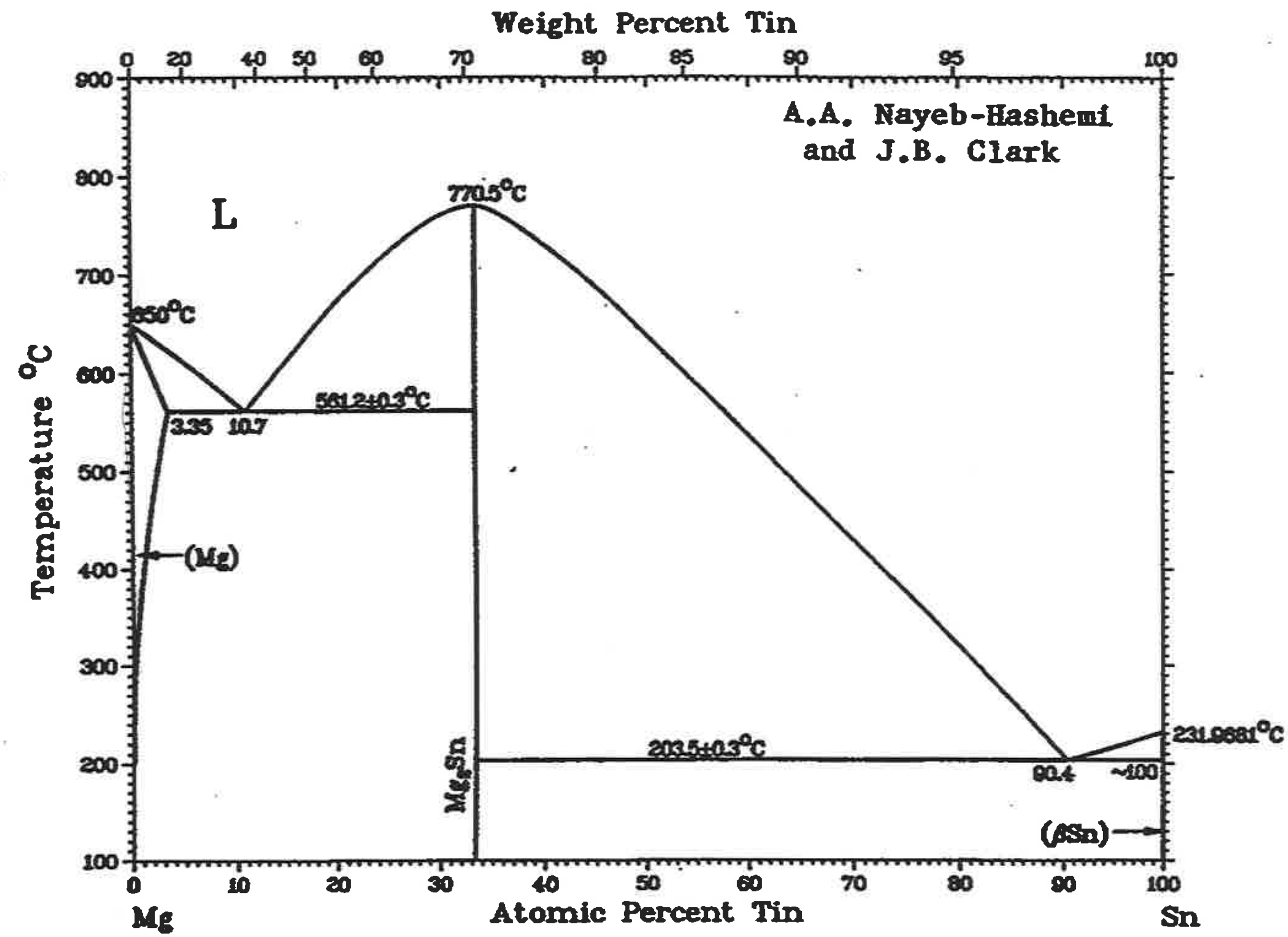

Fig. 15.36 Mg-Sn phase diagram.