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MTE 562	Thermodynamics

Quiz I Solution

Q.1

(5 pts) a.   Define the compressibility factor, Z   chapter 3

(10 pts) b.   Express Cp – Cv for a liquid by using the following empirical equations
(a) and (b) in $Cp - Cv = (\partial V/\partial T)_P [P + (\partial U/\partial V)_T]$

(a) $V = V_0 [1 + a(T - 273)] + bP$;
(b) $U - U_{273} = AT + BV$

Derive the following relations $\left(\frac{\partial V}{\partial T}\right)_P = V_0 a$, and $\left(\frac{\partial U}{\partial V}\right) = B$, and substitute in

$$C_p - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

to obtain

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] = V_0 a (P + B)$$
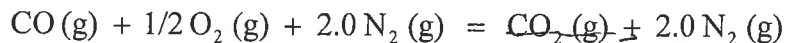
(20 pts) c.   Calculate the adiabatic flame temperature for CO burned completely with
the theoretically sufficient amount of air by using the following data:
ΔH^o_{298} (combustion) = - 282,995 J mol^{-1} of CO,
C_p^o (CO_2) = 44.225 + 0.00878 T J mol^{-1} K^{-1}
C_p^o (N_2) = 28.58 + 0.00376 T J mol^{-1} K^{-1}
Assume that the air contains 20 % O_2 and 80 % N_2.

$CO (g) + 1/2 O_2 (g) + 2.0 N_2 (g) = CO_2 (g) + 2.0 N_2 (g)$

One mole of CO requires 0.5 mole of O_2 carrying with it 2 moles of N_2; therefore,

$$0 = \Delta H^o_{298} + \int_{298}^{T} [C_p^o(CO_2) + 2.0 C_p^o(N_2)] dT$$??

$$= -282,995 + \int_{298}^{T} [101.385 + 0.0163T] dT$$

$$= -313.947 + 101.385T + 0.00815T^2$$

The positive root of this equation is T = 2567 K.

Q.2.

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

(10 pts)　　b.　　Express Heat of Reaction of Pure Iron ($\Delta H_T - \Delta H_{298}$) as a function of Temperature from the attached phase diagram.

Standard reaction enthalpies at different temperatures may be estimated from heat capacities and the reaction enthalpy at some other temperature using a relation defined by Kirchhoff's law.

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int \Delta_r C_p \, dT$$

For pure iron (as shown in the phase diagram) there are three phase transitions:
$\alpha \rightarrow \gamma$ (at 912°C = 1185 K)
$\gamma \rightarrow \delta$ (at 1394°C = 1667 K)
$\delta \rightarrow$ Liquid (at 1538°C = 1811 K)
So, the heat change can be expressed as:

$$\Delta H_T - \Delta H_{298} = \int_{298}^{1185} Cp(\alpha)dT + \Delta H_{1185}(\alpha \rightarrow \gamma) + \int_{1185}^{1667} Cp(\gamma)dT + \Delta H_{1667}(\gamma \rightarrow \delta)$$

$$+ \int_{1667}^{1811} Cp(\delta)dT + \Delta H_{1811}(\delta \rightarrow Liquid) + \int_{1811}^{T} Cp(Liquid)dT$$

(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 x 10^5 N/m² to 4 x 10^4 N/m ². Assuming that the working substance is a kilo mole 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.

a). The initial temperature , T1 , and final temperature T2 are given by T2 = 1473K and T1 = 473 K.

The efficiency , η , of a Carnot heat engine is given by $\eta = 1 - (T1 / T2)$

substitution gives, $\eta = 1 - (473 / 1473) = 0.6789$ or 67.89%

b) The reversible isothermal expansion from (P2, V2, T2) to (P2', V2', T2) is illustrated. We are given that P2 = 5 x 105 N/m2 and P2' = 4 x 104 N/m2. The working substances are 1Kmole of ideal gas. The heat absorbed is

Q2 = RT2 ln (V2'/ V2), we know that P2V2 = RT2 and P2'V2' = RT2, that is

V2'/V2 = P2/P2' = 5 x 105 / 4 x 104 = 12.5

so Q = 8314.3 (1473) ln(12.5) = 3.093 x 107 J.

c).To calculate Q1, use $\eta = 1 - (T1 / T2) = 1 + (Q1 / Q2)$

$1 + (Q1 / Q2) = 1 - (T1 / T2) = 0.6789$, $Q1 / Q2 = -0.3211$

so $Q1 = -9.933 \times 106$ J (i.e., heat is rejected)

Q.3.

(5 pts). a.   Explain the following:
  1. Entropy of phase change
  2. Entropy criteria for reversibility and irreversibility

1. Entropy of phase change

Under equilibrium conditions, the phase change occurs at a constant temperature and pressure. For a pure substance A the phase change from the α-state to the β-state, and the accompanying heat effects are

$$A(\alpha) \Leftrightarrow A(\beta), \text{ and } (Q_{rev})_p = (H\beta - H\alpha)_p$$

the entropy of phase change is

$$(S_\beta - S_\alpha)_p = \left(\frac{Q_{rev}}{T_{\alpha\beta}}\right)_p = \left(\frac{H_\beta - H_\alpha}{T_{\alpha\beta}}\right)_p$$

where $T_{\alpha\beta}$ is the transformation temperature. This statement is often called the Richards rule.

2   Entropy Criteria for reversibility and irreversibility

dSsystem = dQrev/T (reversible i.e. under equilibrium)
            dSsystem > dQirrev/T (irreversible i.e. under spontaneous)
Thus,   dSsystem$\geq^3$ dQ/T
                      dGP,T,W'≤ 0

This relationship is more useful than the others because an overwhelming majority of physical and chemical change occur at constant temperature and pressure.

(10 pts) b.   Show that for an ideal gas, $(\Delta A)_T = (\Delta G)_T$

Integration of dA = -SdT – PdV and dG = -SdT + VdP at constant temperature   gives:

$$(A_2 - A_1)_T = - \frac{\int_{V_1}^{V_2} PdV}{} \qquad \text{and} \qquad (G_2 - G_1)_T = \frac{\int_{P_1}^{P_2} VdP}{}$$

For an ideal gas these equations become:

$$(A_2 - A_1)_T = - \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_1}{V_2} \qquad \text{(ideal gas)}$$

$$(G_2 - G_1)_T = \int_{P_1}^{P_2} \frac{RT}{P} dP = RT \ln \frac{P_2}{P_1} \qquad \text{(ideal gas)}$$

Since $P_2/P_1 = V_1/V_2$ for an ideal gas at constant temperature, give,

$$(A_2 - A_1)_T = (G_2 - G_1)_T \quad \text{(for ideal gases)}$$

(15 pts).c.   Calculate ΔS_T and ΔG_T when 0.21 mole of oxygen and 0.79 mole of nitrogen, each at 1 bar and 25°C are mixed to form a gas mixture at 1 bar. Ideal gas behavior may be assumed for the gases and the mixture.

$$\Delta S_T = - n_1 R \ln (V_1/V) - n_2 R \ln (V_2/V)$$
$$= - 0.21R \ln (0.21/1) - 0.79 R \ln (0.79/1) = 0.514 R$$

Equation 6.24 gives

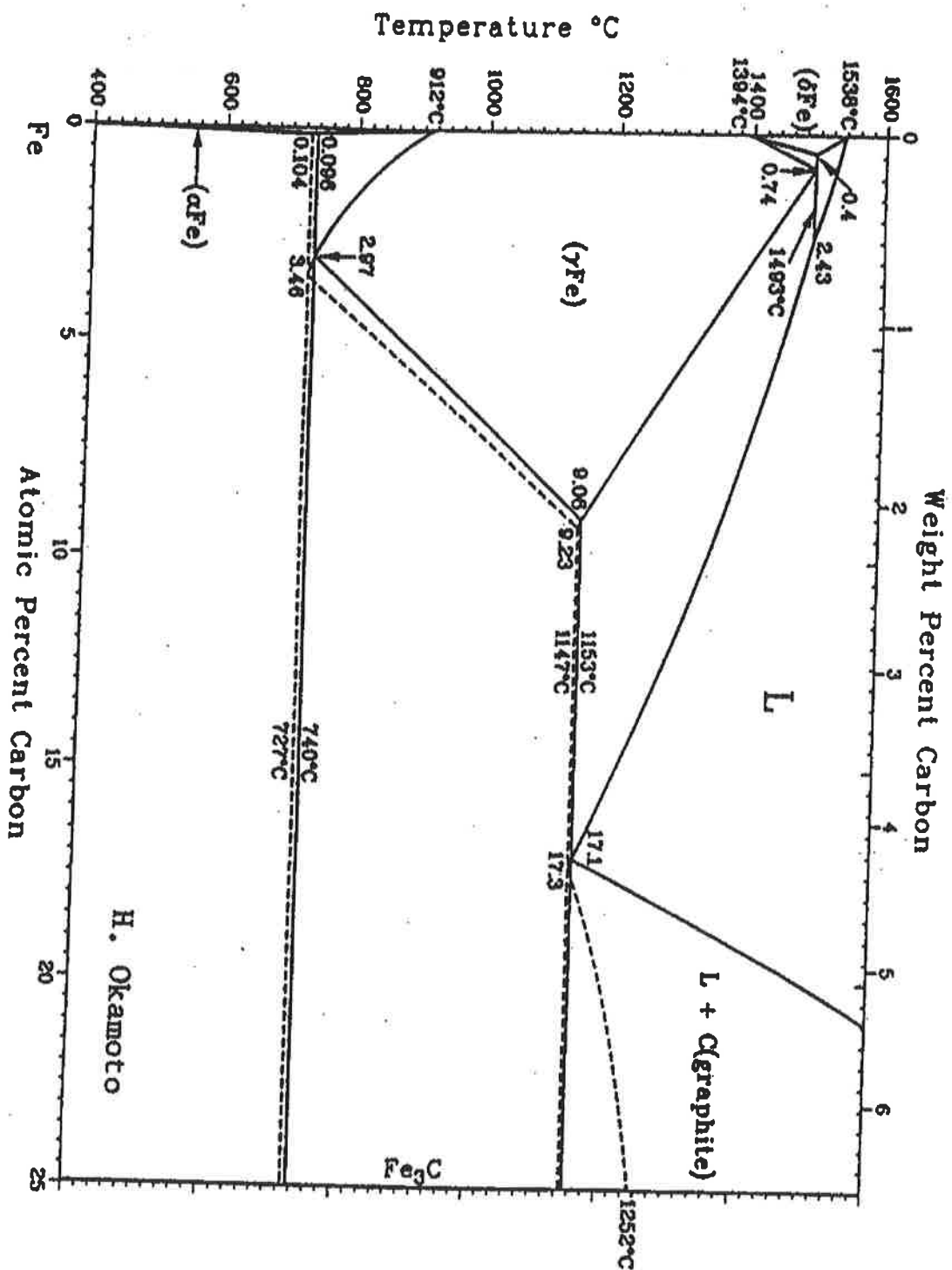$$\Delta G_T = - T \Delta S_T = - 0.514 R \times 298 = -153.25 R$$

Fig. 15.31 C-Fe phase diagram. Broken lines are for Fe-Fe₃C equilibria.