

# Example

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

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MTE 562

Thermodynamics

## Quiz I

Q.1

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

(10 pts) b. Express  $C_p - C_v$  for a liquid by using the following empirical equations

(a) and (b) in  $C_p - C_v = (\partial V / \partial T)_P [P + (\partial U / \partial V)_T]$

$$(a) \quad V = V_0 [1 + a(T - 273)] + bP ;$$

$$(b) \quad U - U_{273} = AT + BV$$

(20 pts) c. Calculate the adiabatic flame temperature for CO burned completely with the theoretically sufficient amount of air by using the following data:

$$\Delta H_{298}^0 (\text{combustion}) = -282,995 \text{ J mol}^{-1} \text{ of CO,}$$

$$C_p^0 (\text{CO}_2) = 44.225 + 0.00878 T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_p^0 (\text{N}_2) = 28.58 + 0.00376 T \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume that the air contains 20 %  $\text{O}_2$  and 80 %  $\text{N}_2$ .

Q.2.

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

(5 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.

(20 pts) c. A Carnot heat engine operates between reservoirs at  $1200^\circ\text{C}$  and  $200^\circ\text{C}$ . The isothermal process at the hotter reservoir consists of an expansion (reversible) from an initial pressure of  $5 \times 10^5 \text{ N/m}^2$  to  $4 \times 10^4 \text{ N/m}^2$ . 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.

Q.3.

(5 pts) a. Explain the following:

1. Entropy of phase change
2. Entropy criteria for reversibility and irreversibility

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

(20 pts) c. One mole of argon at 1 bar and  $T_1$  and 3 moles of helium at 3 bars and at the same temperature are first mixed and then compressed isothermally to 4 bars then heated to  $T_2 = 2T_1$  at constant pressure. What is the entropy change for each step and for the entire process?

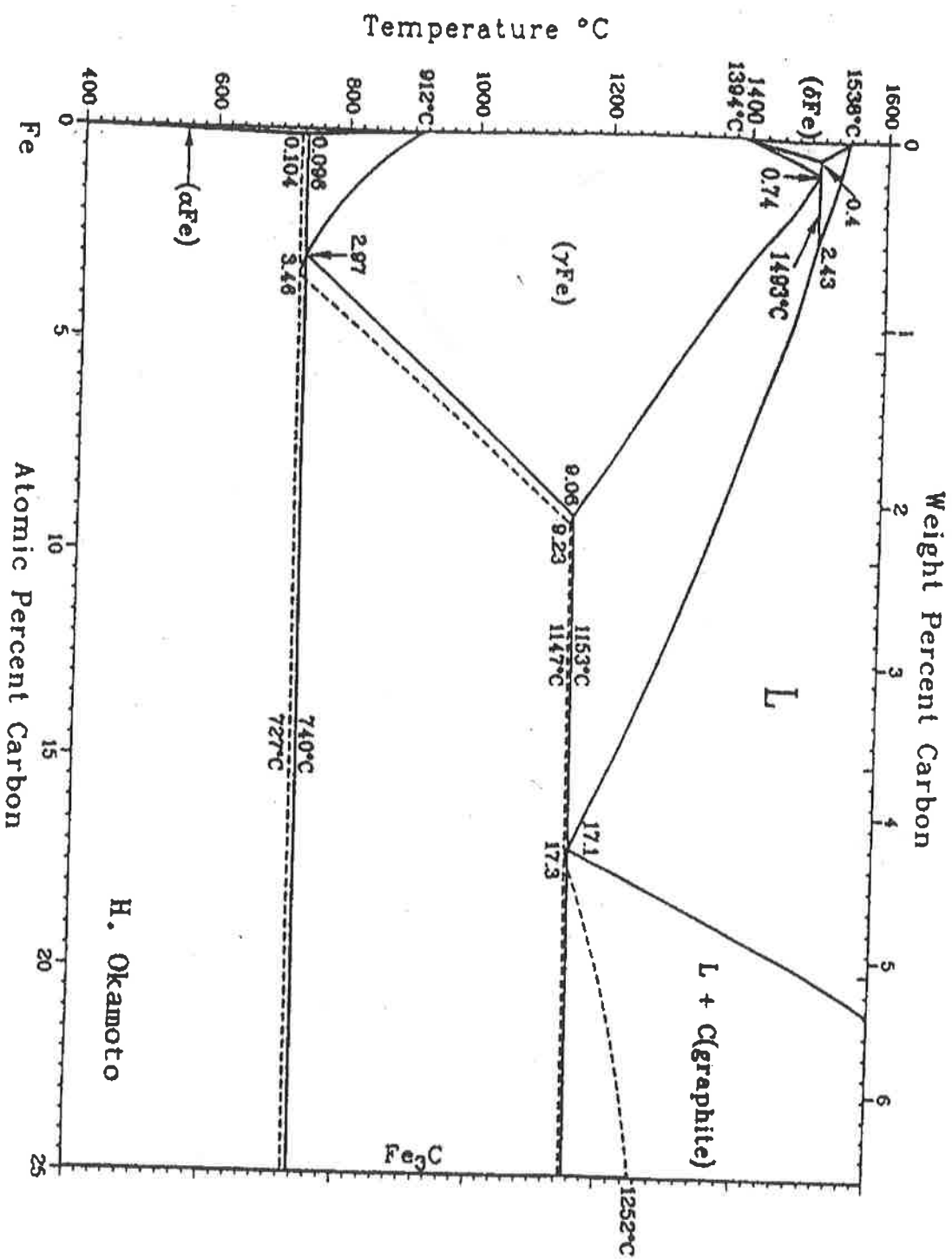


Fig. 15.31 C-Fe phase diagram. Broken lines are for Fe-Fe<sub>3</sub>C equilibria.

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**Quiz I Solution**

Q.1

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

(10 pts) b. Express  $C_p - C_v$  for a liquid by using the following empirical equations

(a) and (b) in  $C_p - C_v = (\partial V / \partial T)_P [P + (\partial U / \partial V)_T]$

$$(a) \quad V = V_0 [1 + a(T - 273)] + bP ;$$

$$(b) \quad U - U_{273} = AT + BV$$

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

$$C_p - C_v = \left(\frac{\partial V}{\partial T}\right)_P \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] = V_0 a (P + B)$$

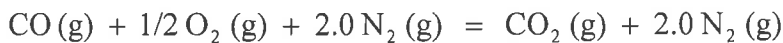
(20 pts) c. Calculate the adiabatic flame temperature for CO burned completely with the theoretically sufficient amount of air by using the following data:

$$\Delta H_{298}^0 (\text{combustion}) = -282,995 \text{ J mol}^{-1} \text{ of CO,}$$

$$C_p^0 (\text{CO}_2) = 44.225 + 0.00878 T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_p^0 (\text{N}_2) = 28.58 + 0.00376 T \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume that the air contains 20 % O<sub>2</sub> and 80 % N<sub>2</sub>.



One mole of CO requires 0.5 mole of O<sub>2</sub> carrying with it 2 moles of N<sub>2</sub>; therefore,

$$\begin{aligned} 0 &= \Delta H_{298}^0 + \int_{298}^T [C_p^0(\text{CO}_2) + 2.0 C_p^0(\text{N}_2)] dT \\ &= -282,995 + \int_{298}^T [101.385 + 0.0163T] dT \\ &= -313.947 + 101.385T + 0.00815T^2 \end{aligned}$$

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.

$$\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \int_{T_1}^{T_2} \Delta_r C_p dT$$

For pure iron (as shown in the phase diagram) there are three phase transitions:

$\alpha \rightarrow \gamma$  (at  $912^\circ\text{C} = 1185 \text{ K}$ )

$\gamma \rightarrow \delta$  (at  $1394^\circ\text{C} = 1667 \text{ K}$ )

$\delta \rightarrow \text{Liquid}$  (at  $1538^\circ\text{C} = 1811 \text{ K}$ )

So, the heat change can be expressed as:

$$\begin{aligned} \Delta H_T - \Delta H_{298} = & \int_{298}^{1185} Cp(\alpha) dT + \Delta H_{1185}(\alpha \rightarrow \gamma) + \int_{1185}^{1667} Cp(\gamma) dT + \Delta H_{1667}(\gamma \rightarrow \delta) \\ & + \int_{1667}^{1811} Cp(\delta) dT + \Delta H_{1811}(\delta \rightarrow \text{Liquid}) + \int_{1811}^T Cp(\text{Liquid}) dT \end{aligned}$$

(20 pts) c. A Carnot heat engine operates between reservoirs at  $1200^\circ\text{C}$  and  $200^\circ\text{C}$ . The isothermal process at the hotter reservoir consists of an expansion (reversible) from an initial pressure of  $5 \times 10^5 \text{ N/m}^2$  to  $4 \times 10^4 \text{ N/m}^2$ . 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,  $T_1$ , and final temperature  $T_2$  are given by  $T_2 = 1473 \text{ K}$  and  $T_1 = 473 \text{ K}$ .

The efficiency,  $\eta$ , of a Carnot heat engine is given by  $\eta = 1 - (T_1 / T_2)$

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

b) The reversible isothermal expansion from  $(P_2, V_2, T_2)$  to  $(P_2', V_2', T_2)$  is illustrated. We are given that  $P_2 = 5 \times 10^5 \text{ N/m}^2$  and  $P_2' = 4 \times 10^4 \text{ N/m}^2$ . The working substances are 1 Kmole of ideal gas. The heat absorbed is

$Q_2 = RT_2 \ln (V_2' / V_2)$ , we know that  $P_2 V_2 = RT_2$  and  $P_2' V_2' = RT_2$ , that is

$$V_2' / V_2 = P_2 / P_2' = 5 \times 10^5 / 4 \times 10^4 = 12.5$$

$$\text{so } Q = 8314.3 (1473) \ln(12.5) = 3.093 \times 10^7 \text{ J.}$$

c). To calculate  $Q_1$ , use  $\eta = 1 - (T_1 / T_2) = 1 + (Q_1 / Q_2)$

$$1 + (Q_1 / Q_2) = 1 - (T_1 / T_2) = 0.6789, \quad Q_1 / Q_2 = -0.3211$$

so  $Q_1 = -9.933 \times 10^6 \text{ J}$  (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  $\alpha$ -state to the  $\beta$ -state, and the accompanying heat effects are

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

the entropy of phase change is

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

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

2 Entropy Criteria for reversibility and irreversibility

$dS_{\text{system}} = dQ_{\text{rev}}/T$  (reversible i.e. under equilibrium)

$dS_{\text{system}} > dQ_{\text{irrev}}/T$  (irreversible i.e. under spontaneous)

Thus,  $dS_{\text{system}} \geq dQ/T$   
 $dG_{P,T,W'} \leq 0$

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:

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

For an ideal gas these equations become:

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

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

Since  $P_2/P_1 = V_1/V_2$  for an ideal gas at constant temperature, give,  
 $(A_2 - A_1)_T = (G_2 - G_1)_T$  (for ideal gases)

(15 pts).c. Calculate  $\Delta S_T$  and  $\Delta G_T$  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.

$$\begin{aligned} \Delta S_T &= -n_1 R \ln (V_1/V) - n_2 R \ln (V_2/V) \\ &= -0.21R \ln (0.21/1) - 0.79 R \ln (0.79/1) = 0.514 R \end{aligned}$$

Equation 6.24 gives

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

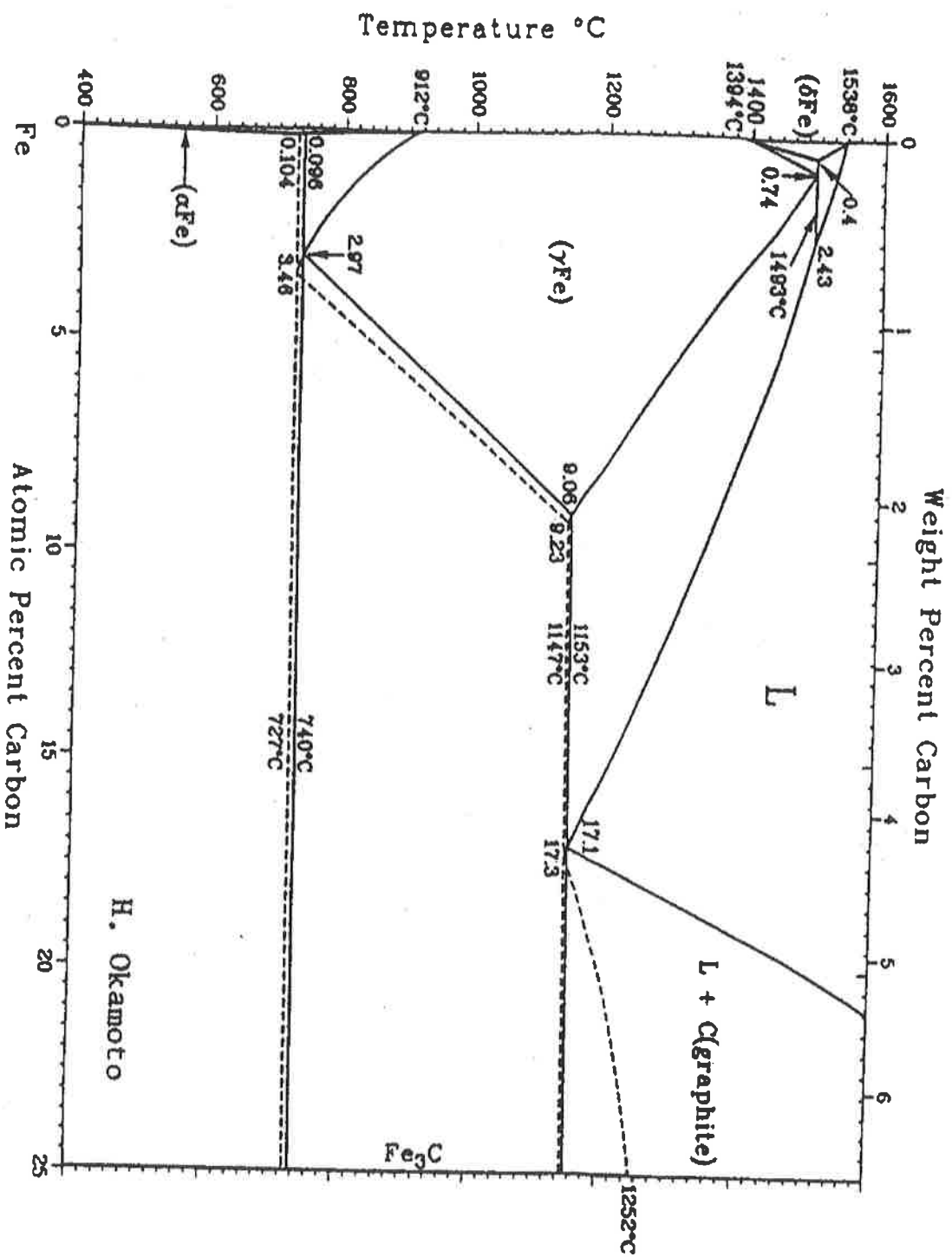


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