Department of Chemical Engineering
NATIONAL INSTITUTE OF TECHNOLOGY CALICUT

Name:————————

Reg. No.————————

Monsoon Semester 2014

End Semester Examination

CH3001 CHEMICAL ENGINEERING THERMODYNAMICS - II

Duration: 3 hour   Maximum Marks: [50]

Instructions: (a) Answer *all* questions (b) Assume any missing data with suitable assumptions

Q.No.

1 (a) Show that for any gas which obeys the van der Waals equation of state   [3]

$\left(P + \frac{a}{v^2}\right)(v - b) = RT$, the relation $\left(\frac{\partial U}{\partial v}\right)_T = \frac{a}{v^2}$ is always true.

(b) Propane gas at 100°C is compressed isothermally from an initial pressure of 10 bar to a   [5]
final pressure of 100 bar. Estimate the change in enthalpy and entropy using Lee-Kesler
data.

(For propane, $T_C = 369.8$ K, $P_C = 42.48$ bar, $\omega=0.152$)

(c) The excess Gibbs energy of a binary liquid mixture at T and P is given by   [4]

$$G^E/_{RT} = (-2.6x_1 - 1.8\,x_2)x_1x_2$$

Find expressions for $\ln\gamma_1$ and $\ln\gamma_2$ at T and P.
G^E is partial molar excess gibbs free energy of the mixture.

2 (a) Estimate the fugacity of liquid water at 40°C and 50 bar.   [3]

(b) Toluene (1) and water (2) are essentially immiscible as liquids. Determine the dew point   [5]
temperatures and the composition of the first drops of liquid formed when vapor
mixtures of these species with mole fractions $z_2 = 0.3$ and $z_2 = 0.6$ are cooled at constant
pressure of 101.33 kPa. Calculate the bubble point temperature and the composition of
the last drop of the vapor in each case?

$$\ln P_1{}^{sat} = 13.9320 - \frac{3056.96}{T + 217.325} \quad \& \quad \ln P_2{}^{sat} = 16.3872 - \frac{3855.70}{T + 230.120}$$

•   P and T are in kPa and °C respectively

3 (a) At P=760 Torr and T = 70°C, three components namely n-Pentane (1), n-Hexane (2) and   [5]
n-Heptane (3) present in a vessel with feed composition z_1=0.3, z_2 =0.35.
   (a) Find whether the system is single phase system or binary phase system
     (b) If the system is a binary phase system at equilibrium, find the compositions
          of liquid and vapor phases.

$$log_{10}P = A - \frac{B}{T+C}, T\ in\ \deg C\ and\ P\ is\ in\ Torr$$

	A	B	C
n- Pentane (1)	6.87632	1075.780	233.205
n- Hexane (2)	6.91058	1189.640	226.280
n- Heptane (3)	6.89386	1264.370	216.640

(b) Nitrogen and hydrogen react to form ammonia in the presence of a catalyst. The reactor in which this reaction is to be run is maintained

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \longrightarrow NH_3$$
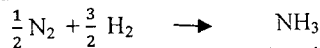
at 450 K and has a sufficiently long residence time that equilibrium is achieved at the reactor exit.

[3] + [3] + [2]

   a. What will be the mole fractions of nitrogen, hydrogen and ammonia exiting the reactor if stoichiometric amounts of nitrogen and hydrogen enter the reactor; which is kept at 4 bar?

   b. What will be the exit mole fractions if the reactor operates at 4 bar and feed consists of equal amounts of nitrogen, hydrogen and an interts diluents?

   c. The reaction is to be run in an isothermal, constant volume reaction vessel with a feed consisting of stoichiometric amounts of nitrogen and hydrogen. The initial pressure in the reactor is 4 bar. What is the pressure in the reactor and the species mole fractions when equilibrium is achieved?

4. (a) Determine the number of independent reactions for the equilibrium mixture of CO, CO_2, H_2, H_2O, and CH_4. [3]

(b) One of the most important industrial reactions is the catalytic production of the synthesis gas : $CH_4 + H_2O \rightarrow CO + 3H_2$
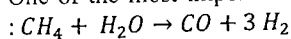
An additional reaction takes place to a significant extent:
$$CO + H_2O \longrightarrow CO_2 + H_2$$
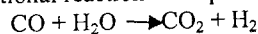
Starting with a ratio of 5 moles of steam to 1 mole of methane, i.e. with an excess of steam, calculate the equilibrium composition of the resulting mixture at 600°C and 1 atm. At this temperature, the equilibrium constants for the first and second reaction are respectively : K_1 = 0.574; K_2 = 2.21. [4]

5. (a) The relation between equilibrium constant K, composition y and pressure P is given as

$$\prod_i (y_i \widehat{\Phi_i})^{v_i} = \left(\frac{P}{P^0}\right)^{-v} K$$, where $\widehat{\Phi_i}$ is the fugacity coefficient of species i and v represents stoichiometric constant. Derive this expression from basics. [3]

(b) A. Explain what are the terms that contribute to molecular potential U. [3]
   B. Sketch the variation of intermolecular potential energy U with molecular separation r. Mark the main points on it and explain. + [2]

(c) How is the second virial coefficient evaluated from statistical mechanics? [2]

Fig. 8.13   Correction term for entropy departure function for pressures greater than $P_r = 1.0$. Chart prepared based on the data of Lee, B.I. and Kesler, M.G., AIChEJ, 21, 510 (1975).
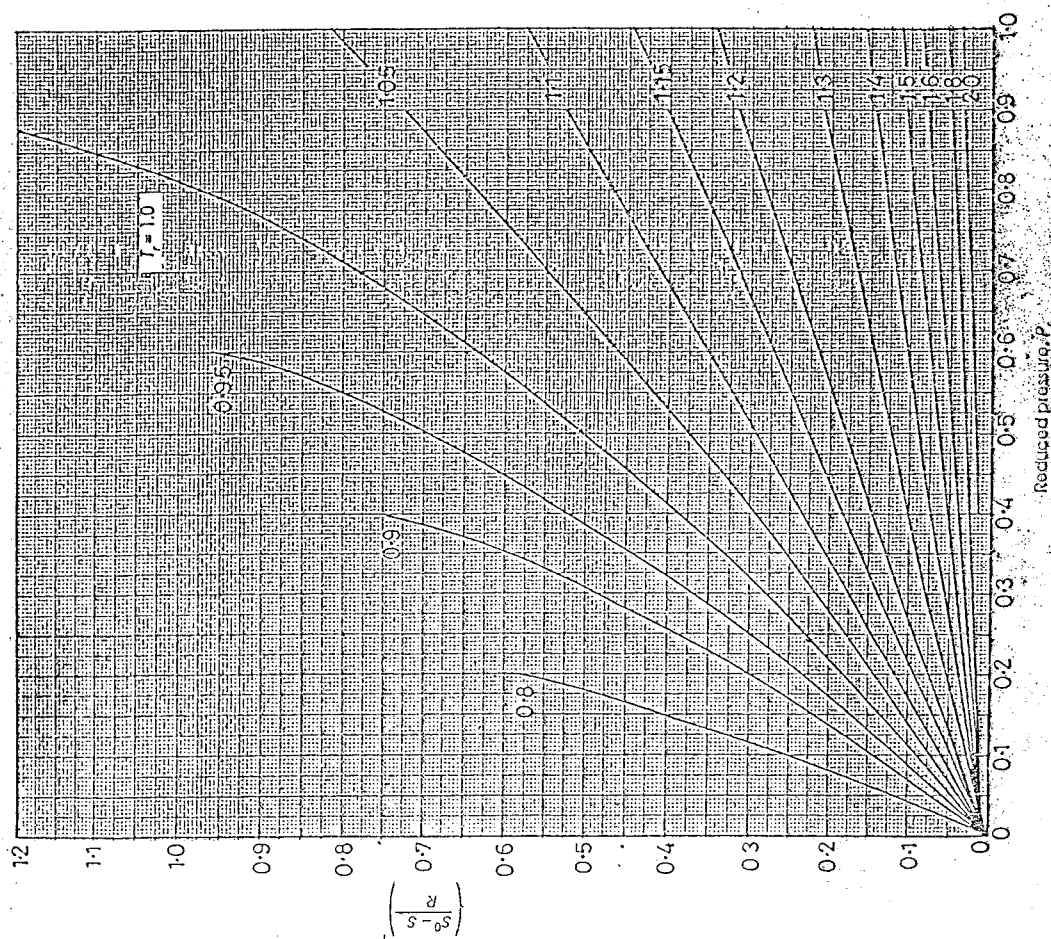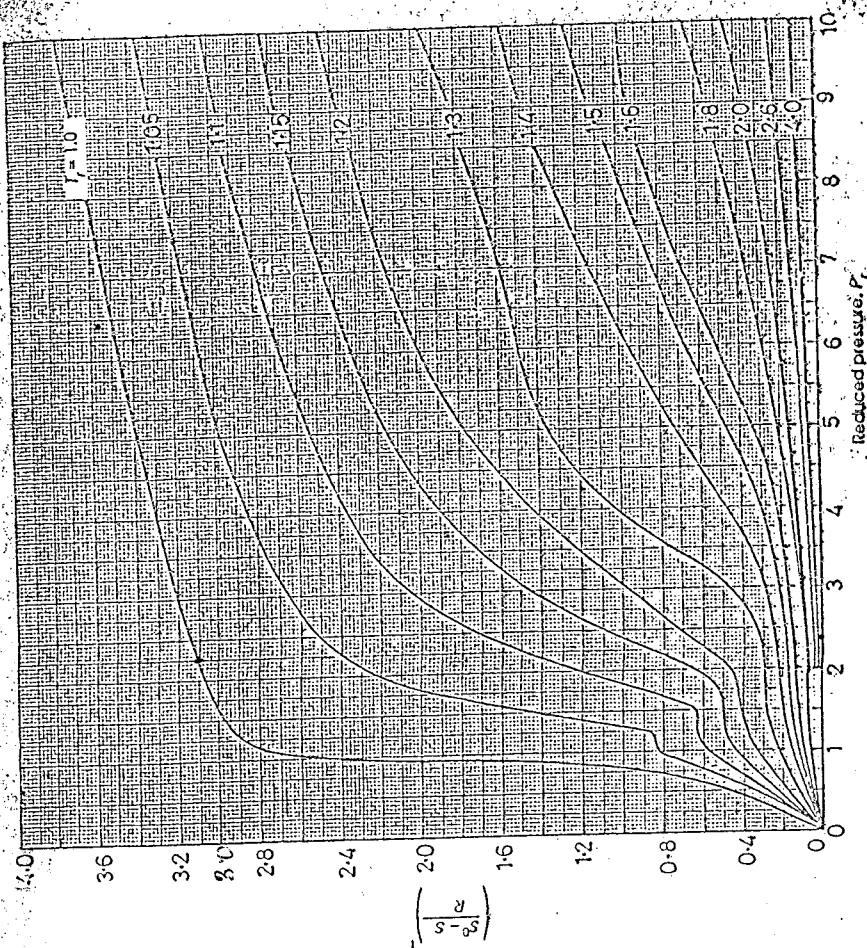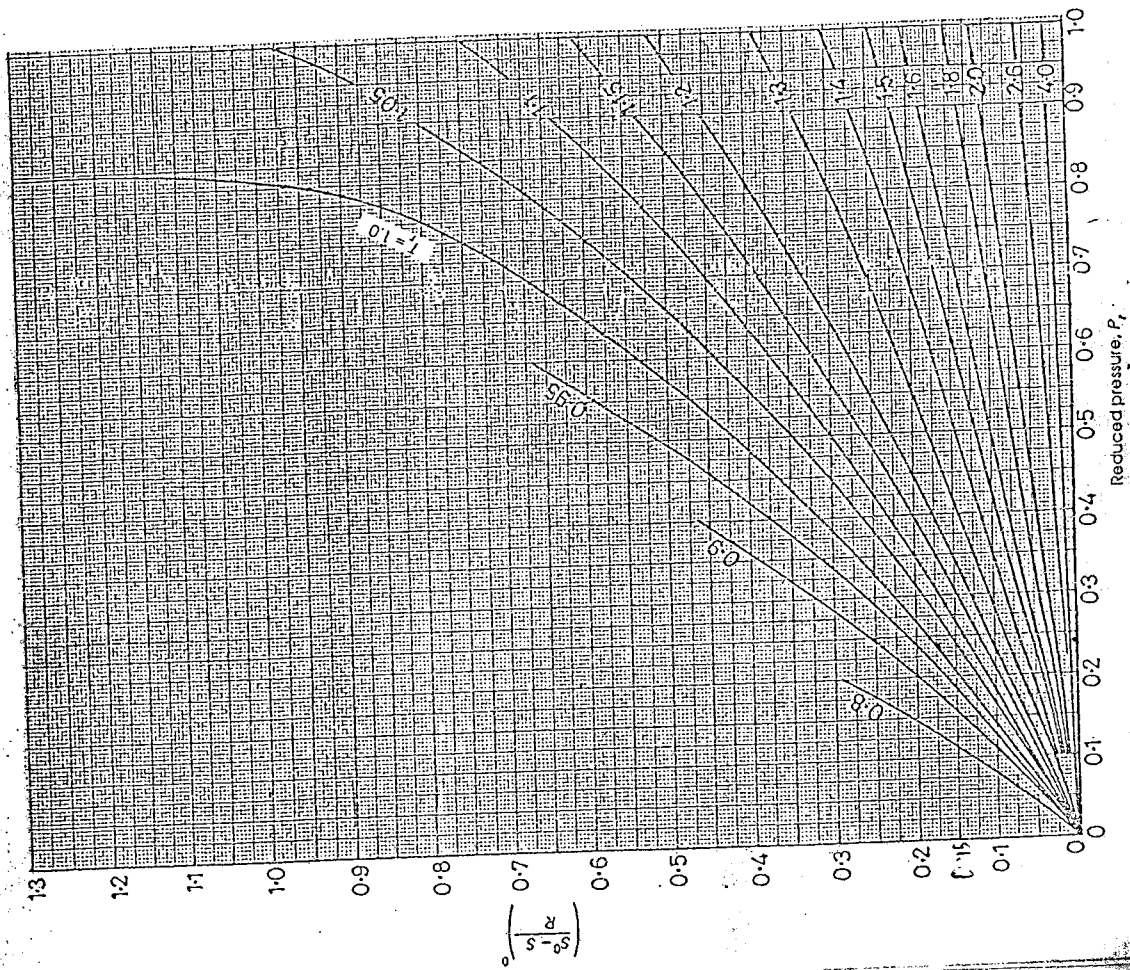

Fig. 8.12   Correction term for entropy departure function for pressures less than $P_r = 1.0$. Chart prepared based on the data of Lee, B.I. and Kesler, M.G., AIChEJ, 21, 510 (1975).

Fig.8.10 Simple fluid entropy departure function for pressures less than $P_r = 1.0$. Chart prepared based on the data of Lee, B.I., and Kesler, M.G., AIChEJ, 21, 510 (1975).
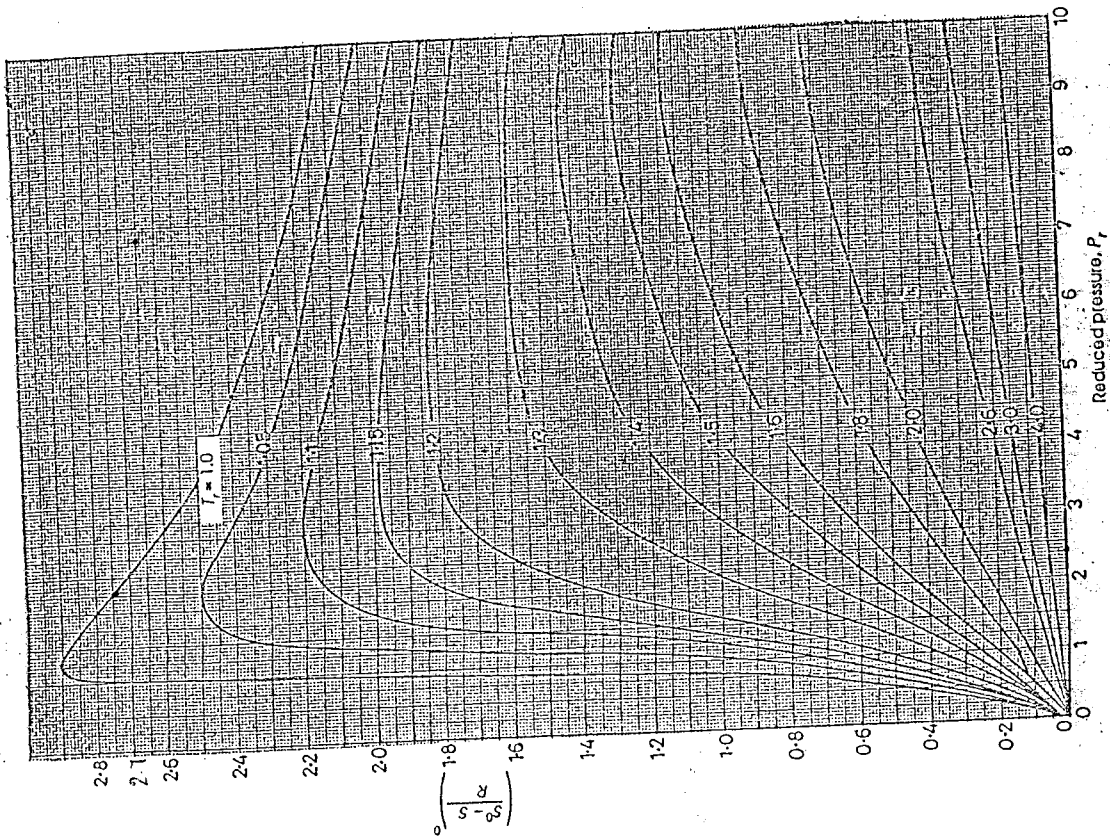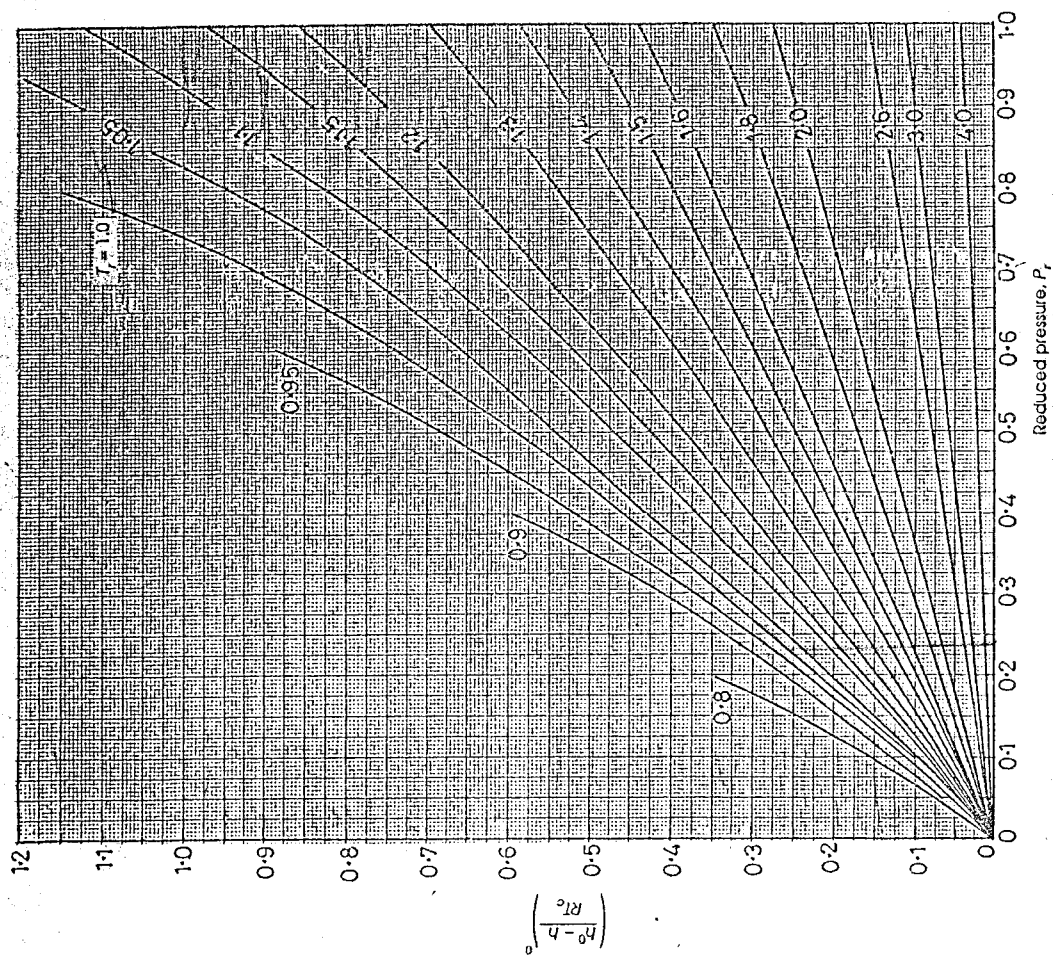

Fig.8.11 Simple fluid entropy departure function for pressures greater than $P_r = 1.0$. Chart prepared based on the data of Lee, B.I. and Kesler, M.G., AIChEJ, 21, 510 (1975).

Fig.8.6 *Simple fluid enthalpy departure function for pressures less than $P_r = 1$. Chart prepared based on the data of Lee, B.I. and Kesler, M.G., AIChEJ, 21, 510 (1975).*
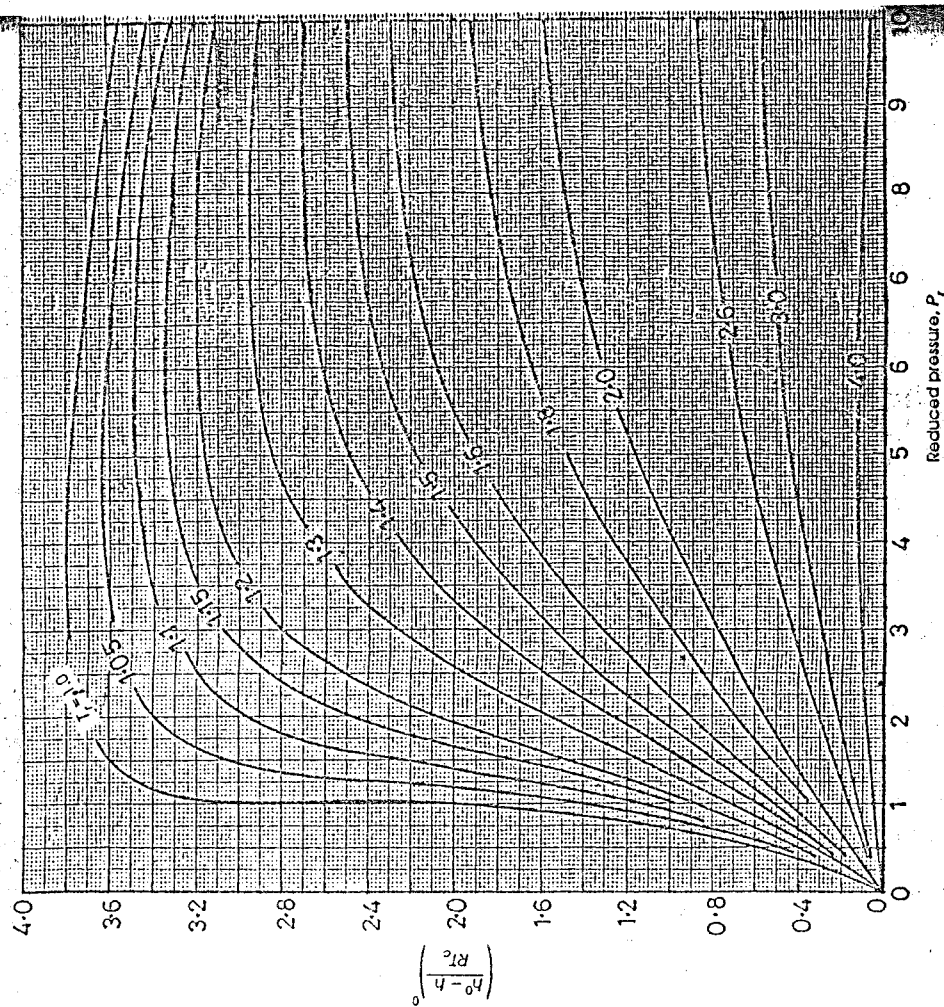

Fig.8.7 *Simple fluid enthalpy departure function for pressures greater than $P_r = 1$. Chart prepared based on the data of Lee, B.I. and Kesler, M.G., AIChEJ, 21, 510 (1975).*
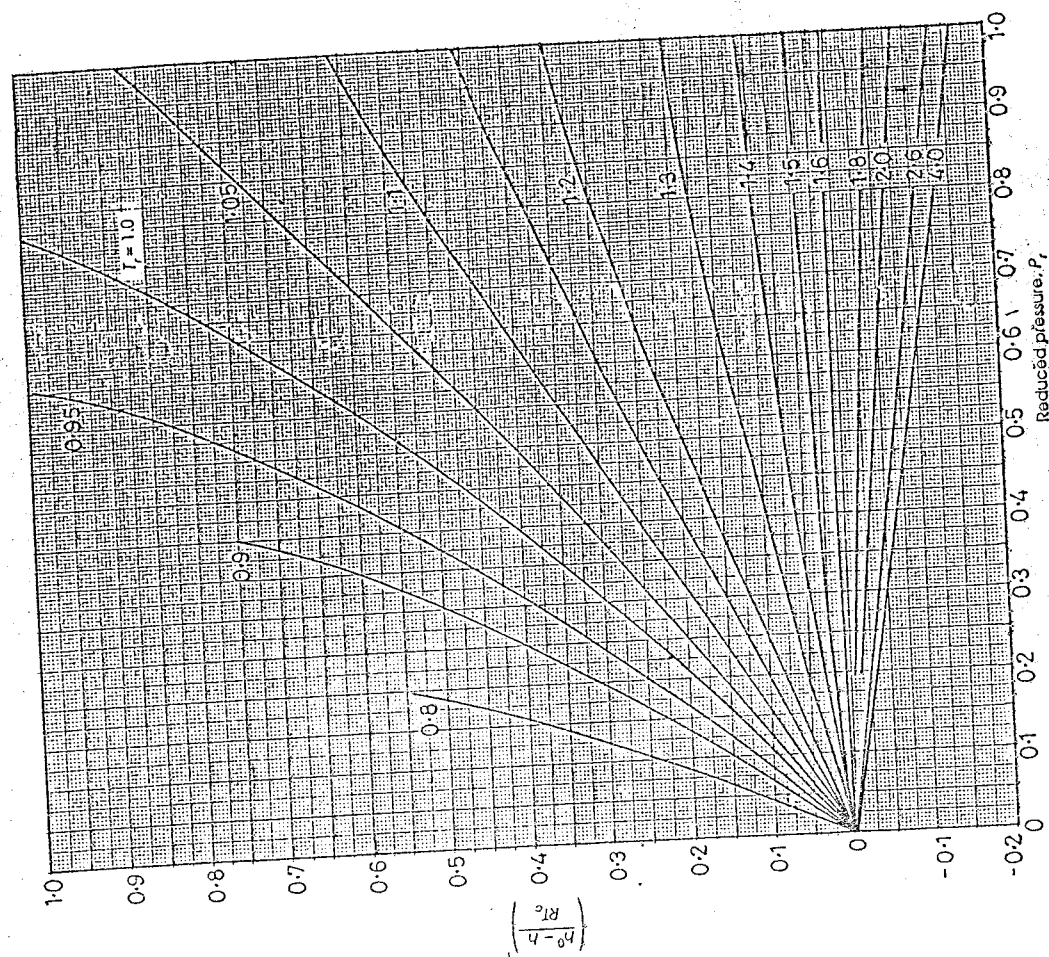
Fig.8.8   Correction term for enthalpy departure function for pressures less than $P_r = 1.0$. Chart prepared based on the data of Lee, B.I. and Kesler, M.G., AIChEJ, 21, 510 (1975).
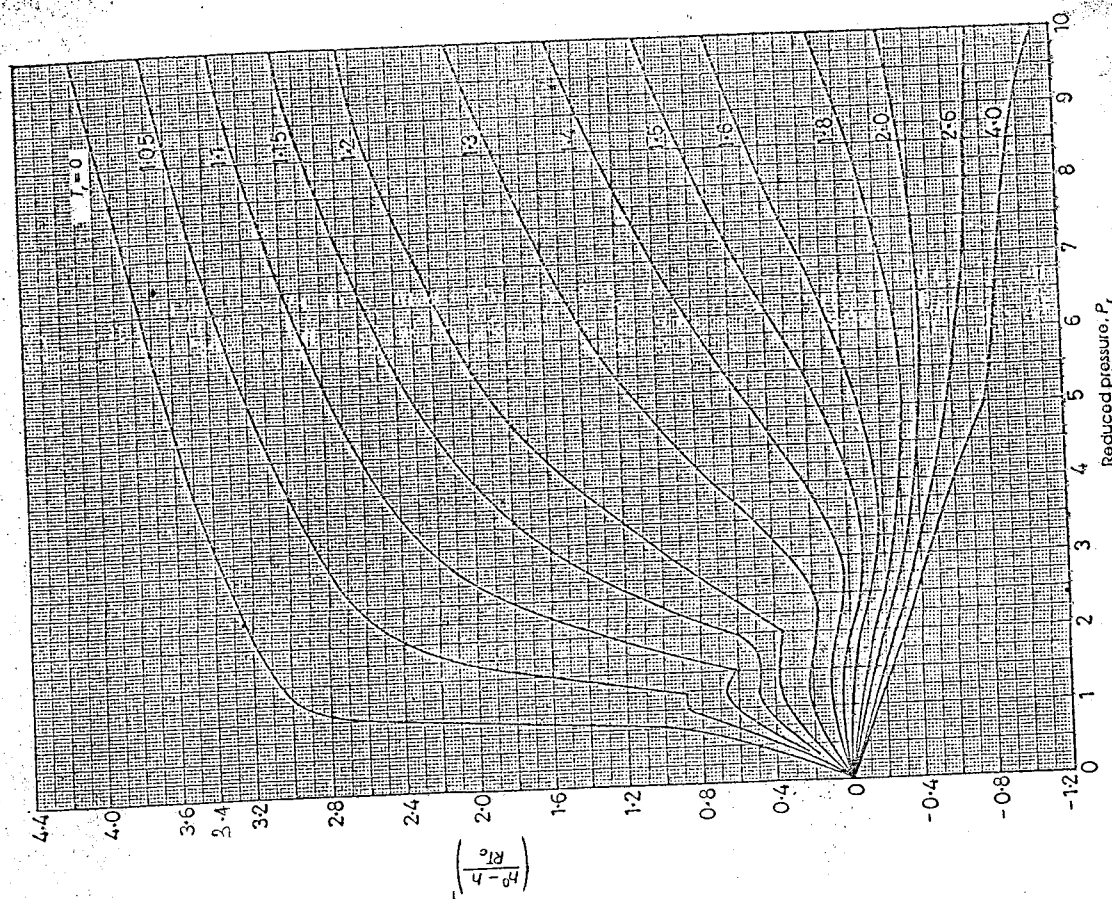
Fig.8.9   Correction term for enthalpy departure function for pressures greater than $P_r = 1.0$. Chart prepared based on the data of Lee, B.I. and Kesler, M.G., AIChEJ, 21, 510 (1975).