Tutorial 1: Thermodynamics of solutions

Exercise 1

For a binary mixture, prove that the partial molar property of constituent 2 is written as follows:

$$\overline{M_2} = M_m + (1 - x_2)\left(\frac{\partial M_m}{\partial x_2}\right)_{P,T,n_1} \text{ and } \overline{M_2} = M_m - x_1\left(\frac{\partial M_m}{\partial x_1}\right)_{P,T,n_1}$$

Exercise 2

The volume of a binary mixture has a molar volume, V, that depends on its composition given by the following expression:

$$V_m = 75x_1 + 95x_2 + 3.7x_1x_2 \left(\frac{cm^3}{mol}\right)$$

1. What is the pure species molar volume for component 1 and component 2.
2. For a mixture with $x_1 = 0.60$.

Determine:
a) the molar volume of the mixture, and b) the partial molar volume of component 1.

Exercise 3

The molar enthalpy of a binary liquid system of species 1 and 2 at fixed T and P is represented by the following equation:

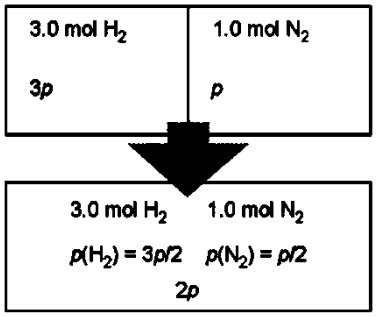
$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

where H is in J/mol

a. determine expressions for $\overline{H_1}$ and $\overline{H_2}$as functions of x_1
b. Numerical values for the pure species enthalpies $H_1^*$and H_2^*
c. Find the expression of (H^E)
d. Numerical values for the partial enthalpies at infinite dilution $\overline{H_1}$ and $\overline{H_2}$

Exercise 4

A container is divided into two equal compartments (figure below). One contains 3.0 mol of H_2 at $25°C$; the other contains 1.0 $mol\ N_2$ $at\ 25^0C$. Calculate the *Gibbs energy* ***of mixing*** when the partition is removed. Assume perfect gas behavior. $P^0 = 1bar$



Exercise 5

For a mixture contains 75% H_2 and 25% N_2 (molar basis) estimate the pseudo critical Temperature and pressure ($P_{pc}and\ T_{pc}$) using Kay's rule.

We give:

For N_2: $T_C = 126.2K\ \ and\ P_C = 33.5atm$

For H_2 $T_C = 33 + 8 = 41K$ *and* $P_C = 12.8 + 8 = 20.8\ atm$

Exercise 6

Determine the specific volume v (m³/kg) of a **methane-ethane gas mixture** at **16 MPa and 250°C**, where the mixture contains: 60 mol% **methane (CH_4)** and 40 mol% **ethane (C_2H_6)**

(a) Assume the mixture ideal (with the mixture gas constant).
(b) Consider a real mixture (the generalized compressibility chart).
(c) determine which method provides the more accurate result and explain why.

Given: $M_{CH4} = 16.04\ g/mol$, $M_{C_2H_6} = 30.07\ g/mol$

Table: Molar mass gas constant and critical point properties-point properties
Chart: Compressibility factor Z as function of P_{pc}

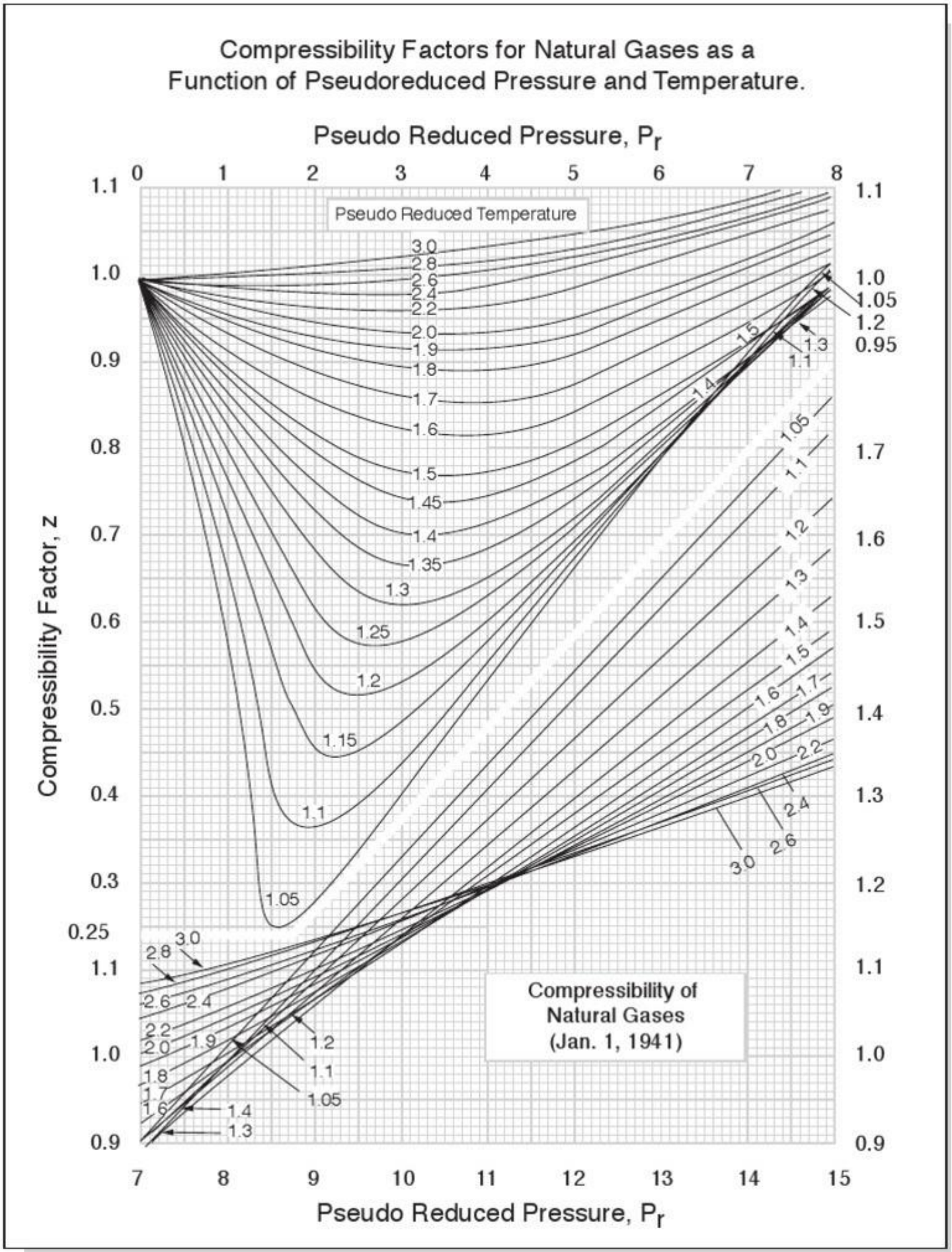
TABLE A–1

Molar mass, gas constant, and critical-point properties

Substance	Formula	Molar mass, *M* kg/kmol	Gas constant, *R* kJ/kg·K*	Critical-point properties: Temperature, K	Pressure, MPa	Volume, m³/kmol
Air	—	28.97	0.2870	132.5	3.77	0.0883
Ammonia	NH_3	17.03	0.4882	405.5	11.28	0.0724
Argon	Ar	39.948	0.2081	151	4.86	0.0749
Benzene	C_6H_6	78.115	0.1064	562	4.92	0.2603
Bromine	Br_2	159.808	0.0520	584	10.34	0.1355
n-Butane	C_4H_{10}	58.124	0.1430	425.2	3.80	0.2547
Carbon dioxide	CO_2	44.01	0.1889	304.2	7.39	0.0943
Carbon monoxide	CO	28.011	0.2968	133	3.50	0.0930
Carbon tetrachloride	CCl_4	153.82	0.05405	556.4	4.56	0.2759
Chlorine	Cl_2	70.906	0.1173	417	7.71	0.1242
Chloroform	$CHCl_3$	119.38	0.06964	536.6	5.47	0.2403
Dichlorodifluoromethane (R-12)	CCl_2F_2	120.91	0.06876	384.7	4.01	0.2179
Dichlorofluoromethane (R-21)	$CHCl_2F$	102.92	0.08078	451.7	5.17	0.1973
Ethane	C_2H_6	30.070	0.2765	305.5	4.48	0.1480
Ethyl alcohol	C_2H_5OH	46.07	0.1805	516	6.38	0.1673
Ethylene	C_2H_4	28.054	0.2964	282.4	5.12	0.1242
Helium	He	4.003	2.0769	5.3	0.23	0.0578
n-Hexane	C_6H_{14}	86.179	0.09647	507.9	3.03	0.3677
Hydrogen (normal)	H_2	2.016	4.1240	33.3	1.30	0.0649
Krypton	Kr	83.80	0.09921	209.4	5.50	0.0924
Methane	CH_4	16.043	0.5182	191.1	4.64	0.0993
Methyl alcohol	CH_3OH	32.042	0.2595	513.2	7.95	0.1180
Methyl chloride	CH_3Cl	50.488	0.1647	416.3	6.68	0.1430
Neon	Ne	20.183	0.4119	44.5	2.73	0.0417
Nitrogen	N_2	28.013	0.2968	126.2	3.39	0.0899
Nitrous oxide	N_2O	44.013	0.1889	309.7	7.27	0.0961
Oxygen	O_2	31.999	0.2598	154.8	5.08	0.0780
Propane	C_3H_8	44.097	0.1885	370	4.26	0.1998
Propylene	C_3H_6	42.081	0.1976	365	4.62	0.1810
Sulfur dioxide	SO_2	64.063	0.1298	430.7	7.88	0.1217
Tetrafluoroethane (R-134a)	CF_3CH_2F	102.03	0.08149	374.2	4.059	0.1993
Trichlorofluoromethane (R-11)	CCl_3F	137.37	0.06052	471.2	4.38	0.2478
Water	H_2O	18.015	0.4615	647.1	22.06	0.0560
Xenon	Xe	131.30	0.06332	289.8	5.88	0.1186

*The unit kJ/kg·K is equivalent to kPa·m³/kg·K. The gas constant is calculated from $R = R_u/M$, where $R_u = 8.31447$ kJ/kmol·K and *M* is the molar mass.

Source: K. A. Kobe and R. E. Lynn, Jr., *Chemical Review* 52 (1953), pp. 117–236; and ASHRAE, *Handbook of Fundamentals* (Atlanta, GA: American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., 1993), pp. 16.4 and 36.1.


Compressibility Factors for Natural Gases as a Function of Pseudoreduced Pressure and Temperature.
Pseudo Reduced Pressure, P_r
Pseudo Reduced Temperature
3.0
2.8
2.6
2.4
2.2
2.0
1.9
1.8
1.7
1.6
1.5
1.45
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
Compressibility Factor, z
Compressibility of Natural Gases (Jan. 1, 1941)
Pseudo Reduced Pressure, P_r