
Problem Set 4

Problem 3.2

A renowned laboratory reports quadruple-point coordinates of 10.2 Mbar and 24.1 deg C for the four-phase equilibrium of allotropic solid forms of the exotic chemical β -maiasmone. Examine the claim using the Gibbs phase rule and provide a plausible explanation for your results.

Problem 3.4

A system of propane and n-butane exists in two-phase vapor/liquid equilibrium at 10 bar and 323 K. The mole fraction of propane is about 0.67 in the vapor phase and about 0.40 in the liquid phase. Additional pure propane is added to the system, which is brought again to equilibrium at the same T and P, with both liquid and vapor phases still present. What is the effect of the addition of propane on the mole fractions of propane in the vapor and liquid phases?

Problem 3.6

Express the volume expansivity (β) and isothermal compressibility (κ) as functions of density and its partial derivatives. For water at 50 °C and 1 bar, $\kappa=44.18 \times 10^{-6} \text{ bar}^{-1}$. To what pressure must water be compressed at 50 °C to change its density by 1%? Assume κ is independent of P.

Problem 3.9

For liquid water the isothermal compressibility is given by

$$\kappa = \frac{c}{V(P+b)},$$

where c and b are functions of temperature only. If 1 kg of water is compressed isothermally and reversibly from 1 to 500 bar at 60 °C, how much work is required? At 60 °C, $b=2,700 \text{ bar}$ and $c=0.125 \text{ cm}^3 \text{ g}^{-1}$.

Problem 3.17

One mole of an ideal gas with $C_p = (7/2)R$ and $C_v = (5/2)R$ expands from $P_1 = 8 \text{ bar}$ and $T_1 = 600 \text{ K}$ to $P_2 = 1 \text{ bar}$ by each of the following paths:

- (a) Constant volume,
- (b) Constant temperature,
- (c) Adiabatically

Assuming mechanical reversibility, calculate W, Q, ΔU , and ΔH for each process. Sketch each path on a single PV diagram.

Problem 3.21

An ideal gas, $C_p = (5/2)R$ and $C_v = (3/2)R$, is changed from $P_1 = 1 \text{ bar}$ and $V_1^t = 12 \text{ m}^3$ to $P_2 = 12 \text{ bar}$ and $V_2^t = 1 \text{ m}^3$ by the following mechanically reversible processes:

- Isothermal compression.
- Adiabatic compression followed by cooling at constant pressure.
- Adiabatic compression followed by cooling at constant volume.
- Heating at constant volume followed by cooling at constant pressure.
- Cooling at constant pressure followed by heating at constant volume.

Calculate Q , W , ΔU^t , and ΔH^t for each of these processes, and sketch the paths of all processes on a single PV diagram.

Problem 3.42

For methyl chloride at 100 degC, the second and third virial coefficients are:

$$B = -242.5 \text{ cm}^3 \text{ mol}^{-1} \text{ and } C = 25,200 \text{ cm}^6 \text{ mol}^{-2}$$

Calculate the work of mechanically reversible, isothermal compression of 1 mole of methyl chloride from 1 bar to 55 bar at 100 degC.

Base your calculations on the following forms of the virial equation:

- $Z = 1 + \frac{B}{V} + \frac{C}{V^2}$
- $Z = 1 + B'P + C'P^2$, where $B' = \frac{B}{RT}$ and $C' = \frac{C-B^2}{(RT)^2}$
- $Z = 1$
- $Z = 1 + \frac{B}{V}$