Chapter 3 Problems

Jian Carlo M. Guevara

Table of Contents

Problem 3.1

How many phase rule variables must be specified to fix the thermodynamic state of each of the following systems?

(a) A sealed flask containing a liquid ethanol-water mixture in equilibrium with its vapor.

(b) A sealed flask containing a liquid ethanol-water mixture in equilibrium with its vapor and nitrogen.

(c) A sealed flask containing ethanol, toluene, and water as two liquid phases plus vapor.

Solution:
Using the phase rule, $F = 2 - \pi + N$.

(a) $N = 2$ and $\pi = 2$ so $\boxed{F = 2}$

(b) $N = 3$ and $\pi = 2$ so $\boxed{F = 3}$

(c) $N = 3$ and $\pi = 3$ so $\boxed{F = 2}$

Problem 3.2

A renowned laboratory reports quadruple-point coordinates of 10.2 Mbar and 24.1 °C for four-phase equilibrium of allotropic solid forms of the exotic chemical β-miasmone. Evaluate the claim.

Solution:

$$F = 2 - \pi + N$$

If $N = 1$ and $\pi = 4$, the phase rule suggests that $F = -1$. The claim is impossible unless there are other components present in the system.

Problem 3.3

A closed, nonreactive system contains species 1 and 2 in vapor/liquid equilibrium. Species 2 is a very light gas, essentially insoluble in the liquid phase. The vapor phase contains both species 1 and 2. Some additional moles of species 2 are added to the system, which is then restored to its initial temperature T and pressure P. As a result of the process, does the total number of moles of liquid increase, decrease, or remain unchanged?

Solution:

$$N = 2, \qquad \pi = 2 \qquad \rightarrow \qquad F = 2.$$

With constant temperature and pressure, the system's equilibrium is constrained. Introducing species 2 increases y_2 and decreases y_1. Therefore, to maintain the original vapor equilibrium, liquid species 1 must evaporate, resulting in a decrease in the total moles of liquid.

Problem 3.4

A system comprised of chloroform, 1,4-dioxane, and ethanol exists as a two-phase vapor/liquid system at 50 °C and 55 kPa. After the addition of some pure ethanol, the system can be returned to two-phase equilibrium at the initial T and P. In what respect has the system changed, and in what respect has it not changed?

Solution:

$$N = 3, \qquad \pi = 2 \qquad \rightarrow \qquad F = 3$$

The addition of ethanol increases the y_{EtOH} and x_{EtOH} of the system thus decreasing $(y_{\mathrm{EtOH}})'$ and $(x_{EtOH})'$. Since only two *independent* intensive variables were changed, the number of phases will remain unchanged.

Problem 3.5

For the system described in Prob. 3.4:

(a) How many phase-rule variables in addition to T and P must be chosen so as to fix the compositions of both phases?

(b) If the temperature and pressure are to remain the same, can the overall composition of the system be changed (by adding or removing material) without affecting the compositions of the liquid and vapor phases?

Solution:

(a) 3 degrees of freedom.

(b) One more intensive variable (mole fraction of one component) must be fixed in order to fix the intensive state of the system.

Problem 3.6

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

Solution:

$$\kappa \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\int \kappa \, dP = \int -\rho \, d \left(\frac{1}{\rho} \right)$$

let $u = 1/\rho$ $\rightarrow$ $\rho \, d \, (1/\rho) = 1/u \, d \, (u)$:

$$\kappa \Delta P = -\ln \left(\frac{u_2}{u_1} \right) = \ln \left(\frac{\rho_2}{\rho_1} \right)$$

$$\left(44.18 \times 10^{-6} \right) (P_2 - 1) = \ln (1.01)$$

$$\boxed{P_2 = 226 \text{ bar}}$$

Problem 3.7

Generally, volume expansivity β and isothermal compressibility κ depend on T and P. Prove that:

$$\left(\frac{\partial \beta}{\partial P} \right)_T = - \left(\frac{\partial \kappa}{\partial T} \right)_P$$

Solution:

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \qquad \kappa \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$dV = \frac{1}{d\beta}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{d\kappa}\left(\frac{\partial V}{\partial P}\right)_T$$

$$-\left(\frac{\partial \kappa}{\partial T}\right)_P = \left(\frac{\partial \beta}{\partial P}\right)_T$$

Problem 3.8

The Tait equation for liquids is written for an isotherm as:

$$V = V_0\left(1 - \frac{AP}{B+P}\right)$$

where V is molar or specific volume, V_0 is the hypothetical molar or specific volume at zero pressure, and A and B are positive constants. Find an expression for the isothermal compressibility consistent with this equation.

Solution:

$$\kappa \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$= \frac{-1}{V}\frac{d}{dP}\left[V_0\left(1 - \frac{AP}{B+P}\right)\right]$$

after differentiation:

$$= \frac{-1}{V}\left[V_0 A (B+P)^{-1} - V_0 (AP)(B+P)^{-2}\right]$$

simplification:

$$\boxed{\kappa = \frac{-V_0}{V}\left[\frac{A}{B+P} - \frac{AP}{(B+P)^2}\right]}$$

Problem 3.9

For liquid water the isothermal compressibility is given by:

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

5

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, $b = 2700$ bar and $c = 0.125$ cm^3 g^{-1}.

Solution:

$$W = -\int_{V_1}^{V_2} P \, dV$$

$$\kappa \equiv \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$dV = -\kappa V \, dP$$

$$dV = -\frac{c}{P+b} \, dP$$

$$W = \frac{c}{3} \left(500^3 - 1 \right) \ \text{bar} \, \text{cm}^3 \, \text{g}^{-1} \times 1000\text{g} \times 10^2 \text{kPa} \, \text{bar}^{-1} \times 0.01^3 \text{m}^3 \, \text{cm}^{-3}$$

$$\boxed{W = 1562500\text{kJ}}$$

Problem 3.10

Calculate the reversible work done in compressing 1 ft^3 of mercury at a constant temperature of 32°F from 1(atm) to 3000(atm). The isothermal compressibility of mercury at 32°F is:

$$\kappa(\text{atm})^{-1} = 3.9 \times 10^{-6} - 0.1 \times 10^{-9} P(\text{atm})$$

Solution:

$$W = -\int_{V_1}^{V_2} P \, dV$$

$$\kappa = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$dV = -\kappa V \, dP$$

$$W = -\int_{P_1}^{P_2} - \left(3.9 \times 10^{-6} - 0.1 \times 10^{-9} P \right) V \, dP$$

$$W = 0.0112461 \ \text{atm} \, \text{ft}^3 \times 101325 \ \text{Pa} \, \text{atm}^{-1} \times 3.28^{-3} \ \text{m}^3 \, \text{ft}^{-3}$$

$$\boxed{W = 32.29 \ \text{J}}$$

Problem 3.11

Five kilograms of liquid carbon tetrachloride undergo a mechanically reversible, isobaric change at 1 bar during which the temperature changes from 0 °C to 20 °C. Determine ΔV, W, Q, ΔH, and ΔU. The properties for liquid carbon tetrachloride at 1 bar and 0 °C may be assumed independent of temperature: $\beta = 1.2 \times 10^{-3}$ K^{-1}, $C_P = 0.84$ kJ kg^{-1} K^{-1}, and $\rho = 1590$ kg m^{-3}.

Solution:

(a) for ΔV

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Delta V = \frac{\beta}{\rho} \times \Delta T$$

$$\boxed{\Delta V = 1.509 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}}$$

(b) for W

$$W = -P\Delta V$$

$$W = -100000 \left(1.509 \times 10^{-5} \right)$$

$$\boxed{W = -1.509 \text{ J kg}^{-1}}$$

(c) for Q and ΔH

$$Q = \Delta H = C_P \Delta T$$

$$= 0.84 \times (20)$$

$$\boxed{Q = \Delta H = 16.8 \text{ kJ kg}^{-1}}$$

(d) for ΔU

$$\Delta U = Q + W$$

$$\Delta U = 16800 - 1.509$$

$$\boxed{\Delta U \approx 16.8 \text{ kJ kg}^{-1}}$$

Problem 3.12

Various species of hagfish, or slime eels, live on the ocean floor, where they burrow inside other fish, eating them from the inside out and secreting copious amounts of slime. Their skins are widely used to make eelskin wallets and accessories. Suppose a hagfish is caught in a trap at a depth of 200 m below the ocean surface, where the water temperature is 10 °C, then brought to the surface where the temperature is 15 °C. If the isothermal compressibility and volume expansivity are assumed constant and equal to the values for water,

$$(\beta = 10^{-4} \text{K}^{-1} \text{ and } \kappa = 4.8 \times 10^{-5} \text{ bar}^{-1})$$

what is the fractional change in the volume of the hagfish when it is brought to the surface?

Solution:

$$\frac{dV}{V} = \beta dT - \kappa dP$$

$$\frac{\Delta V}{V} = \beta \Delta T - \kappa \Delta P$$

$$\frac{\Delta V}{V} = 10^{-4} \left(10 - 15\right) - 4.8 \times 10^{-5} \left(1000 \cdot 9.81 \cdot (0 - 200) \cdot 10^{-5}\right)$$

$$\boxed{\frac{\Delta V}{V} = 4.4176 \times 10^{-4} \text{ volume change per unit volume of the hagfish.}}$$

It will expand.

Table 3.2: Volumetric Properties of Liquids at 20°C

Table 3.2 provides the specific volume, isothermal compressibility, and volume expansivity of several liquids at 20°C and 1 bar[25] for use in Problems 3.13 to 3.15, where β and κ may be assumed constant.

Molecular Formula	Chemical Name	Specific Volume $V/\text{L}\cdot\text{kg}^{-1}$	Isothermal Compressibility $\kappa/10^{-5} \text{ bar}^{-1}$	Volume Expansivity $\beta/10^{-3} \text{ }°\text{C}^{-1}$
$C_2H_4O_2$	Acetic Acid	0.951	9.08	1.08
C_6H_7N	Aniline	0.976	4.53	0.81
CS_2	Carbon Disulfide	0.792	9.38	1.12
C_6H_5Cl	Chlorobenzene	0.904	7.45	0.94
C_6H_{12}	Cyclohexane	1.285	11.3	1.15
$C_4H_{10}O$	Diethyl Ether	1.401	18.65	1.65
C_2H_6O	Ethanol	1.265	11.19	1.40
$C_4H_8O_2$	Ethyl Acetate	1.110	11.32	1.35
C_8H_{10}	m-Xylene	1.157	8.46	0.99
CH_4O	Methanol	1.262	12.14	1.49
CCl_4	Tetrachloromethane	0.628	10.5	1.14
C_7H_8	Toluene	1.154	8.96	1.05
$CHCl_3$	Trichloromethane	0.672	9.96	1.21

Problem 3.13

For one of the substances in Table 3.2, compute the change in volume and work done when one kilogram of the substance is heated from 15°C to 25°C at a constant pressure of 1 bar.

Solution:

$$\Delta V = V \left(\beta \Delta T - \kappa \cancel{\Delta P} \right)$$
$$W = -P\Delta V$$

$$\Delta V = \begin{bmatrix} 1.03e-05 \\ 7.91e-06 \\ 8.87e-06 \\ 8.50e-06 \\ 1.48e-05 \\ 2.31e-05 \\ 1.77e-05 \\ 1.50e-05 \\ 1.15e-05 \\ 1.88e-05 \\ 7.16e-06 \\ 1.21e-05 \\ 8.13e-06 \end{bmatrix} \text{m}^3 \qquad W = \begin{bmatrix} -1.03 \\ -0.79 \\ -0.89 \\ -0.85 \\ -1.48 \\ -2.31 \\ -1.77 \\ -1.50 \\ -1.15 \\ -1.88 \\ -0.72 \\ -1.21 \\ -0.81 \end{bmatrix} \text{J}$$

Problem 3.14

For one of the substances in Table 3.2, compute the change in volume and work done when one kilogram of the substance is compressed from 1 bar to 100 bar at a constant temperature of 20°C.

Solution:

$$dV = -V\kappa dP$$

$$W = \int_{V_1}^{V_2} -P\,dV$$

$$W = \frac{V\kappa}{2}\left(P_2^2 - P_1^2\right)$$

$$\Delta V = \begin{bmatrix} -8.55e-06 \\ -4.38e-06 \\ -7.35e-06 \\ -6.67e-06 \\ -1.44e-05 \\ -2.59e-05 \\ -1.40e-05 \\ -1.24e-05 \\ -9.69e-06 \\ -1.52e-05 \\ -6.53e-06 \\ -1.02e-05 \\ -6.63e-06 \end{bmatrix} \text{m}^3 \quad W = \begin{bmatrix} 4.32e-04 \\ 2.21e-04 \\ 3.71e-04 \\ 3.37e-04 \\ 7.26e-04 \\ 1.31e-03 \\ 7.08e-04 \\ 6.28e-04 \\ 4.89e-04 \\ 7.66e-04 \\ 3.30e-04 \\ 5.17e-04 \\ 3.35e-04 \end{bmatrix} \text{J}$$

Problem 3.15

For one of the substances in Table 3.2, compute the final pressure when the substance is heated from 15°C and 1 bar to 25°C at constant volume.

Solution:

$$P_2 = P_1 + \frac{\beta\Delta T}{\kappa}$$

$$P_2 = \begin{bmatrix} 2.19 \\ 2.79 \\ 2.19 \\ 2.26 \\ 2.02 \\ 1.88 \\ 2.25 \\ 2.19 \\ 2.17 \\ 2.23 \\ 2.09 \\ 2.17 \\ 2.21 \end{bmatrix} \text{ bar}$$

Problem 3.16

A substance for which κ is a constant undergoes an isothermal, mechanically reversible process from initial state (P_1, V_1) to final state (P_2, V_2), where V is molar volume.

(a) Starting with the definition of κ, show that the path of the process is described by:
$$V = A(T) \exp(-\kappa P)$$

(b) Determine an exact expression which gives the isothermal work done on 1 mol of this constant-κ substance.

Solution:

(a)

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$
$$\kappa dP = \frac{-dV}{V}$$
$$\kappa P = -\ln V + A$$
$$\boxed{V = A(T) e^{-\kappa P}}$$

(b) Derivation of the previous answer to solve for P in $W = -PdV$, then

solving for the integral:

$$P = \frac{1}{\kappa} \ln\left(\frac{A\left(T\right)}{V}\right)$$

$$W = -\int_{V_1}^{V_2} \frac{1}{\kappa} \ln\left(\frac{A\left(T\right)}{V}\right) dV$$

$$W = \frac{1}{\kappa}\left[V \ln\left(\frac{V}{A\left(T\right)}\right) - \int \frac{1}{A\left(T\right)} dV\right]_{V_1}^{V_2}$$

$$\boxed{W = \Delta V \ln\frac{V_2}{V_1} - \frac{\Delta V}{A\left(T\right)}}$$

Problem 3.17

One mole of an ideal gas with $C_P = \frac{7}{2}R$ and $C_V = \frac{5}{2}R$ 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.

Solution:

(a)

$$Q = \Delta U = C_V \Delta T$$

$$\Delta H = \Delta U + \Delta\left(PV\right)$$

$$\frac{P_1}{P_2} = \frac{T_1}{T_2} \rightarrow T_2 = 75\text{ K}$$

$$V = \frac{RT}{P} \rightarrow V = 6.235854 \times 10^{-3}\text{ m}^3$$

$$\boxed{\begin{array}{c} W = 0 \\ Q = \Delta U = -10.9\,\text{kJ} \\ \Delta H = -15.3\,\text{kJ} \end{array}}$$

(b)

$$W = -RT \ln\frac{V_2}{V_1} = -RT \ln\frac{P_1}{P_2}$$

$$W = -Q$$

12

$$\Delta H = \Delta U = 0$$
$$W = -10.4 \text{ kJ}$$
$$Q = 10.4 \text{ kJ}$$

(c)

$$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}$$
$$T_2 = 331.227 \text{ K}$$
$$\Delta U = W = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

$$Q = 0$$
$$\Delta U = W = -5.59 \text{ kJ mol}^{-1}$$
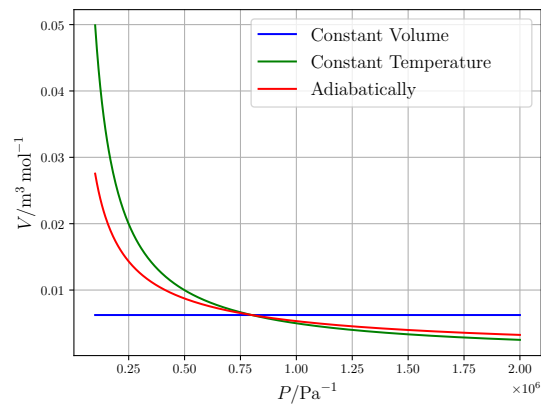$$\Delta H = -7.82 \text{ kJ mol}^{-1}$$

Figure 1: PV diagram showing the three different processes as described in Problem 3.17.

Problem 3.18

One mole of an ideal gas with $C_P = \frac{5}{2}R$ and $C_V = \frac{3}{2}R$ expands from $P_1 = 6$ bar and $T_1 = 800$ K to $P_2 = 1$ bar by each of the following paths:

(a) Constant volume;

(b) Constant temperature;

(c) Adiabatically.

13

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

Solution:

(a)

$$\Delta U = Q = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
$$T_2 = 133.33 \text{ K}$$

$$\boxed{\begin{array}{c} W = 0 \\ \Delta U = Q = -8.31 \text{ kJ mol}^{-1} \\ \Delta H = -13.86 \text{ kJ mol}^{-1} \end{array}}$$

(b)

$$W = -RT \ln \frac{P_1}{P_2}$$
$$Q = -W$$

$$\boxed{\begin{array}{c} W = -11.92 \text{ kJ mol}^{-1} \\ Q = 11.92 \text{ kJ mol}^{-1} \end{array}}$$

(c)

$$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}$$
$$T_2 = 390.69 \text{ K}$$
$$\Delta U = W = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

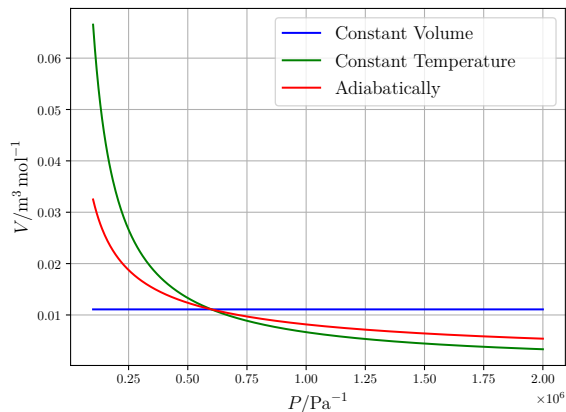$$\boxed{\begin{array}{c} Q = 0 \\ \Delta U = W = -5.10 \text{ kJ mol}^{-1} \\ \Delta H = -8.51 \text{ kJ mol}^{-1} \end{array}}$$

Figure 2: PV diagram showing the three different processes as described in Problem 3.18.

Problem 3.19

An ideal gas initially at $600\,\mathrm{K}$ and $10\,\mathrm{bar}$ undergoes a four-step mechanically reversible cycle in a closed system. In step 12, pressure decreases isothermally to $3\,\mathrm{bar}$; in step 23, pressure decreases at constant volume to $2\,\mathrm{bar}$; in step 34, volume decreases at constant pressure; and in step 41, the gas returns adiabatically to its initial state. Take $C_P = \frac{7}{2}R$ and $C_V = \frac{5}{2}R$.

(a) Sketch the cycle on a PV diagram.

(b) Determine (where unknown) both T and P for states 1, 2, 3, and 4.

(c) Calculate Q, W, ΔU, and ΔH for each step of the cycle.

Solution:

(a) Figure 3

(b)

    i. State 2: The path from state 1 to state 2 is isothermal so $T_2 = 600$ K

    ii. State 3: Solving for T_3 using the ideal gas equation yields 400 K

    iii. State 4: The path from state 3 to state 4 is isobaric so $P_2 = 2$ bar. Using the fact that state 4 to state 1 is adiabatic, we can use

$$TP^{(1-\gamma)/\gamma} = \text{constant}$$
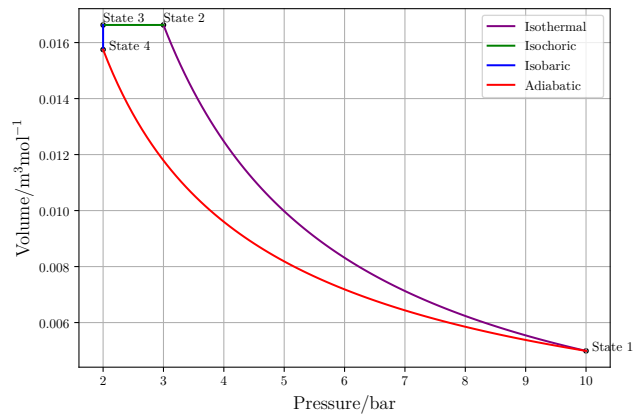
to solve for T_4 which is 378.83 K

15

Figure 3: PV graph of the four-step cycle as described in Problem 3.19.

(c)

i. Path 1

$$Q = -W$$
$$Q = P\,dV$$
$$Q = RT \ln \frac{P_1}{P_2}$$

$$\boxed{\begin{aligned} \Delta H = \Delta U &= 0 \\ Q &= 6.01 \text{ kJ mol}^{-1} \\ W &= -6.01 \text{ kJ mol}^{-1} \end{aligned}}$$

ii. Path 2

$$Q = \Delta U$$
$$Q = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

$$\boxed{\begin{aligned} W &= 0 \\ Q = \Delta U &= -4.16 \text{ kJ mol}^{-1} \\ \Delta H &= -5.82 \text{ kJ mol}^{-1} \end{aligned}}$$

iii. Path 3

$$Q = \Delta H$$
$$Q = C_P \Delta T$$
$$\Delta U = C_V \Delta T$$
$$W = (C_V - C_P)(\Delta T)$$

$$\boxed{\begin{aligned} Q = \Delta H &= -0.62 \text{ kJ mol}^{-1} \\ \Delta U &= -0.44 \text{ kJ mol}^{-1} \\ W &= -0.18 \text{ kJ mol}^{-1} \end{aligned}}$$

Problem 3.20

An ideal gas initially at $300\,\text{K}$ and $1\,\text{bar}$ undergoes a three-step mechanically reversible cycle in a closed system. In step 12, pressure increases isothermally to $5\,\text{bar}$; in step 23, pressure increases at constant volume; and in step 31, the gas returns adiabatically to its initial state. Take $C_P = \frac{7}{2}R$ and $C_V = \frac{5}{2}R$.

(a) Sketch the cycle on a PV diagram.

(b) Determine (where unknown) V, T, and P for states 1, 2, and 3.

(c) Calculate Q, W, ΔU, and ΔH for each step of the cycle.

Solution:

(a) Figure 4

(b)

i. State 1: Use the ideal gas equation to determine V which is $0.0249\,\text{m}^3/\text{mol}$

ii. State 2: The path from state 1 to state 2 is isothermal therefore $T_2 = 300$ K. Determining V_2 from the ideal gas equation yields $0.05\,\text{m}^3/\text{mol}$

iii. State 3: The path from state 2 to state 3 is isochoric therefore $V_3 = 0.05\,\text{m}^3/\text{mol}$. The path from state 3 to state 1 is adiabatic so we can use one of the adiabatic equations; I will use this

$$PV^\gamma = \text{constant}$$

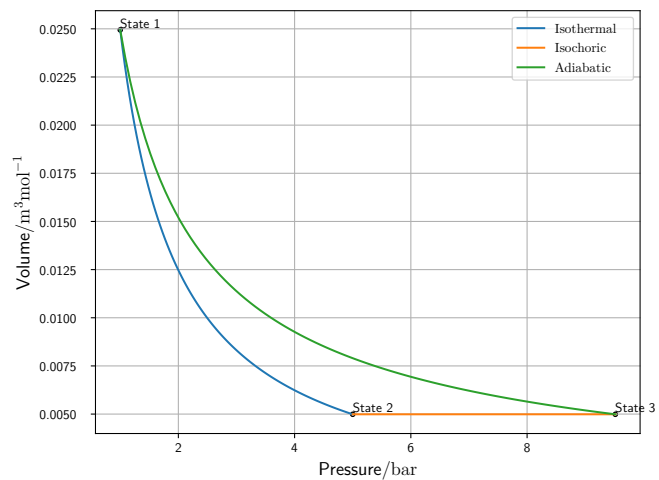to get the value of P_3 which is about 0.38 bar. T_3 can be solved by using the ideal gas law which is about 226 K

Figure 4: PV graph of the three-step cycle as described in Problem 3.20.

(c)   i. Path 1

$$Q = -W$$

$$Q = RT \ln \frac{P_1}{P_2}$$

$$\boxed{\begin{array}{c} \Delta H = \Delta U = 0 \\ Q = -4.01 \text{ kJ mol}^{-1} \\ W = 4.01 \text{ kJ mol}^{-1} \end{array}}$$

ii. Path 2

$$Q = \Delta U$$
$$Q = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

$$\boxed{\begin{array}{c} W = 0 \\ Q = \Delta U = -1.54 \text{ kJ mol}^{-1} \\ \Delta H = -2.15 \text{ kJ mol}^{-1} \end{array}}$$

iii. Path 3

$$W = \Delta U$$
$$W = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

18

$$Q = 0$$
$$W = \Delta U = 1.54 \text{ kJ mol}^{-1}$$
$$\Delta H = 2.15 \text{ kJ mol}^{-1}$$

Problem 3.21

The state of an ideal gas with $C_P = \frac{5}{2}R$ is changed from $P_1 = 1\,\text{bar}$ and $V_1 = 12\,\text{m}^3$ to $P_2 = 12\,\text{bar}$ and $V_2 = 1\,\text{m}^3$ by the following mechanically reversible processes:

(a) Isothermal compression.

(b) Adiabatic compression followed by cooling at constant pressure.

(c) Adiabatic compression followed by cooling at constant volume.

(d) Heating at constant volume followed by cooling at constant pressure.

(e) Cooling at constant pressure followed by heating at constant volume.

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

Solution:

(a)

$$T = \frac{PV}{R}$$
$$T = 144334.86 \text{ K}$$
$$Q = -W$$
$$Q = RT \ln \frac{P_1}{P_2}$$

$$\Delta H = \Delta U = 0$$
$$Q = -2982.06 \text{ kJ mol}^{-1}$$
$$W = 2982.06 \text{ kJ mol}^{-1}$$

ΔU and ΔH for all processes is 0.

(b)

$$V_{1.5} = \left(\frac{P_1 V_1^{\gamma}}{P_{1.5}} \right)^{1/\gamma}$$
$$V_{1.5} = 2.70 \text{ m}^3/\text{mol}$$

After some derivation for the work:

$$W = W_{1 \to 1.5} + W_{1.5 \to 2}$$

$$W_{1 \to 1.5} = -Rc \int_{V_1}^{V_{1.5}} V^{-\gamma} \, dV \qquad \text{where} \qquad c = P_1 V_1^{\gamma}$$

$$W_{1.5 \to 2} = -P_2 \left(V_2 - V_{1.5} \right)$$

$$Q = -W$$

$$\boxed{\begin{aligned} W &= 2040.25 \text{ kJ mol}^{-1} \\ Q &= -2040.25 \text{ kJ mol}^{-1} \end{aligned}}$$

(c)

$$P_{1.5} = \frac{P_1 V_1^{\gamma}}{V_{1.5}^{\gamma}}$$

$$P_{1.5} = 62.898 \text{ bar}$$

$$T_{1.5} = \frac{P_{1.5} V_{1.5}}{R}$$

$$T_{1.5} = 756528.668 \text{ K}$$

$$T_2 = \frac{P_2 V_2}{R}$$

$$T_2 = 144334.8569 \text{ K}$$

$$W = W_{1 \to 1.5} = -c \int_{V_1}^{V_{1.5}} V^{-\gamma} \, dV \qquad \text{where} \qquad c = P_1 V_1^{\gamma}$$

$$Q_{1 \to 1.5} = -W_{1 \to 1.5}$$

$$Q_{1.5 \to 2} = C_V \Delta T$$

$$Q = Q_{1 \to 1.5} + Q_{1.5 \to 2}$$

$$\boxed{\begin{aligned} W &= -1.645 \times 10^7 \text{ kJ mol}^{-1} \\ Q &= 1.644 \times 10^7 \text{ kJ mol}^{-1} \end{aligned}}$$

(d)

$$T = \frac{PV}{R}$$

$$T_1 = T_2 = 144334.8569 \text{ K}$$

$$T_{1.5} = 1732018.282 \text{ K}$$

$$Q_{1 \to 1.5} = C_V (T_{1.5} - T_1)$$

$$Q_{1.5 \to 2} = C_P (T_2 - T_{1.5})$$

$$Q = Q_{1 \to 1.5} + Q_{1.5 \to 2}$$

$$W = -P(V_2 - V_{1.5})$$

$$\boxed{\begin{array}{c} Q = -13200 \text{ kJ mol}^{-1} \\ W = 13200 \text{ kJ mol}^{-1} \end{array}}$$

It is much easier to do $W = -P(V_2 - V_{1.5})$ and solving for $Q = -W$.

(e)

$$W = -P(V_{1.5} - V_1)$$
$$Q = -W$$

$$\boxed{\begin{array}{c} W = -1100 \text{ kJ mol}^{-1} \\ Q = 1100 \text{ kJ mol}^{-1} \end{array}}$$
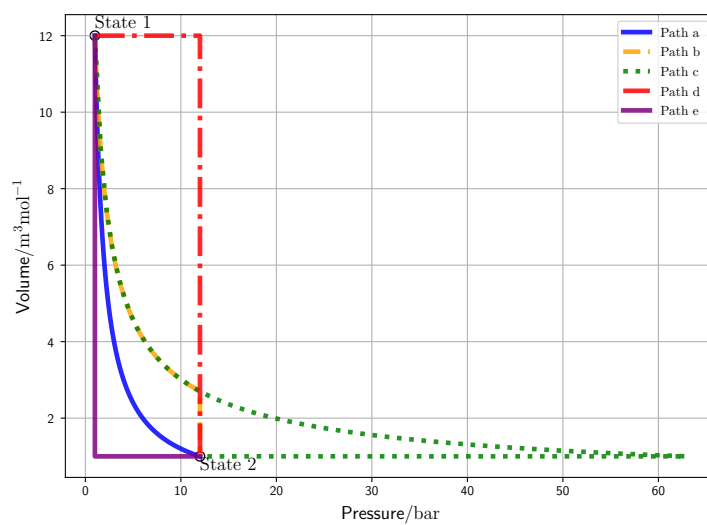

Figure 5: PV graph of the five different paths as described in Problem 3.21.