

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.

Solution

Something is wrong with the claim because it appears to violate the phase rule. The phase rule states that $F = 2 - \pi + N$. Since the number of phases is 4 and the number of chemically distinct species is 1, then $F = 2 - 4 + 1 = -1$. So either the number of chemically distinct species is greater than 1 or the number of phases is less than 4.

Problem 3.4

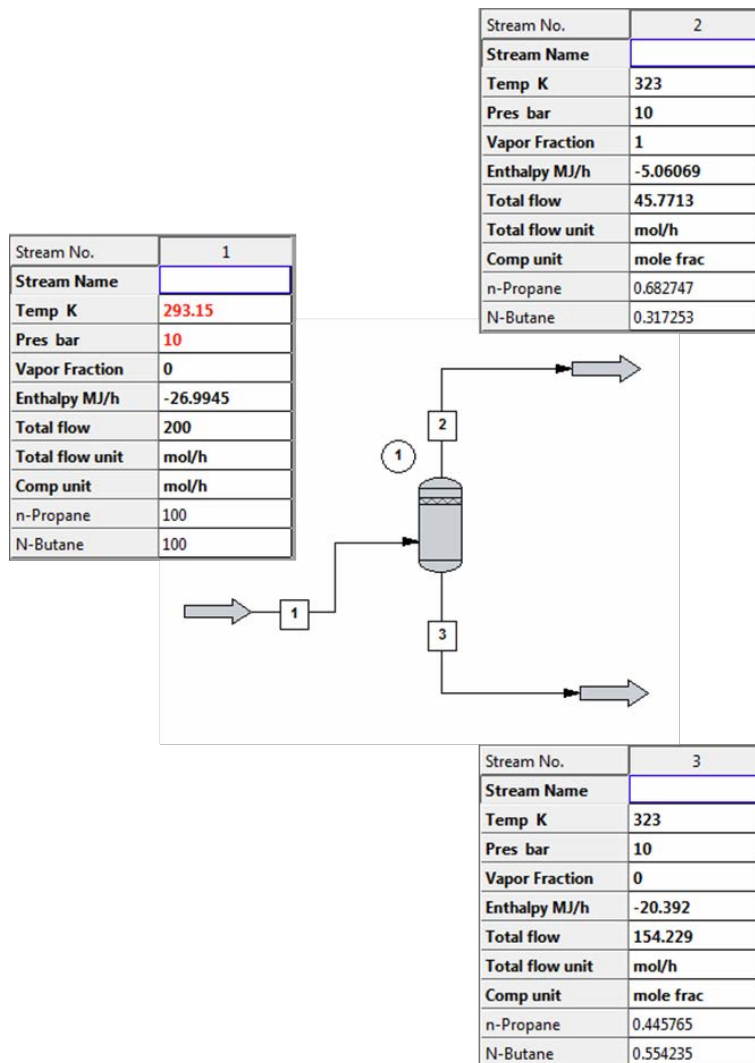
A system of propane and n-butane exists in two-phase vapor/liquid equilibrium at 10 bar and 323 K. The mole fraction of propane is about 0.67 in the vapor phase and about 0.40 in the liquid phase. Additional pure propane is added to the system, which is brought again to equilibrium at the same T and 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?

Solution

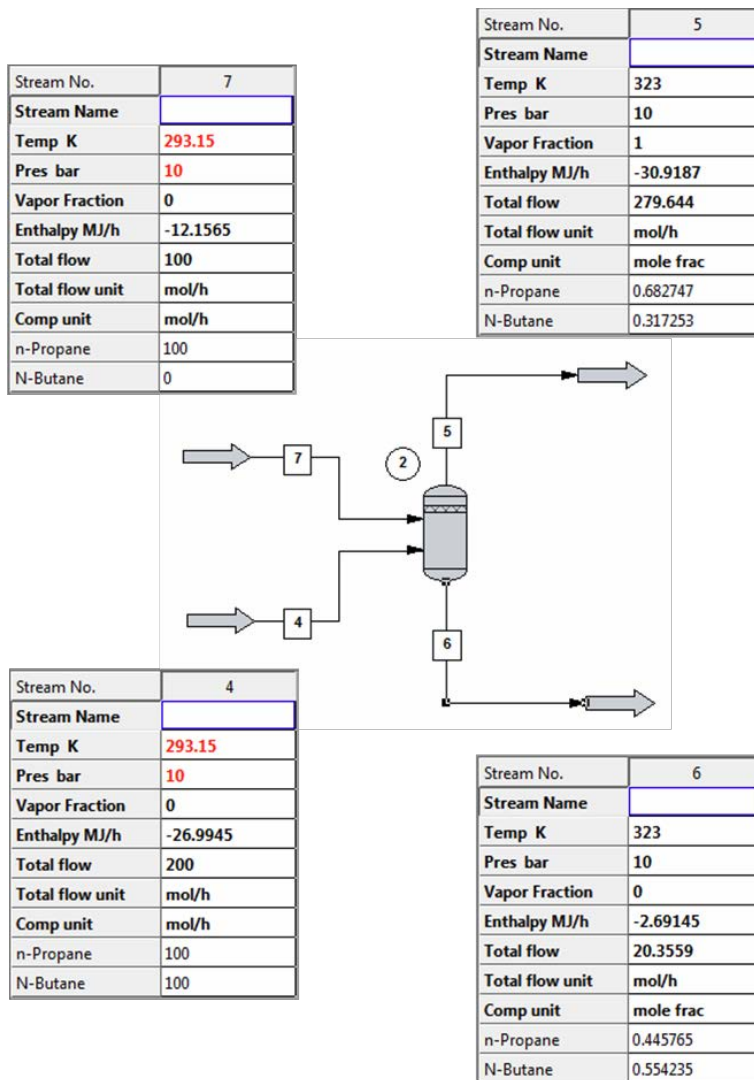
The phase rule states that $F = 2 - \pi + N = 2 - 2 + 2 = 2$, which means that the system has two degrees of freedom. Specifying T and P satisfies the degrees of freedom and fixes the *intensive* state of the system. As long as the system is returned to the same T and P, all intensive variables must also be the same. Since mole fractions are intensive properties, the phase rule predicts that the mole fractions must be unchanged. //ANS

This is illustrated in CHEMCAD below (not needed to answer the question).

Case 1: Flash at original specifications



Case 2: Adding more propane



Comparison of stream 2 with stream 5 shows that the mole fractions are the same. But something had to change. Notice that the total flows are different. Total flow is an extensive property.

The same observation results from comparing streams 3 and 6. The mole fractions are the same but the total flows are different.

(This will only be true as long as there are two 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 degC and 1 bar, $\kappa = 44.18 \times 10^{-6} \text{ bar}^{-1}$. To what pressure must water be compressed at 50 degC to change its density by 1%? Assume κ is independent of P.

Solution

Part 1

Express β and κ as functions of density and its partial derivatives. The key to this part of the problem is to use equations 3.2-3.5 as a guide. In those equations, $V=V(T,P)$. Just repeat the four equations using $\rho = \rho(T,P)$:

$$\begin{aligned} d\rho &= \left(\frac{\partial \rho}{\partial T} \right)_P dT + \left(\frac{\partial \rho}{\partial P} \right)_T dP \\ \beta &\equiv -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \\ \kappa &\equiv +\frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \\ \frac{d\rho}{\rho} &= -\beta dT + \kappa dP \end{aligned}$$

(*Cadets tend to put the wrong signs on β and κ .)

We must use a negative sign in front of $\partial \rho / \partial T$ is negative, so the negative sign makes β positive. As temperature goes up, density goes down, so $\partial \rho / \partial T$ is negative. This property was originally derived from molar volume, where $\beta = (\partial V / \partial T)_P / V$. This derivative is always positive because molar volume increases as temperature increases.

When repeating the derivation with density, it is desirable to keep β the same since the property itself does not change, so we use the negative sign to compensate for the negative derivative.

Likewise, when derived from density, κ uses a positive sign in the derivative because density increases as pressure increases, so $(\partial \rho / \partial P)_T$ is positive. In the original derivation from V, we used a negative sign because $(\partial V / \partial P)_T$ is negative. That is, the molar volume decreases as pressure increases.

Part 2

Calculate the pressure required to change the density by 1%

$$\begin{aligned} \kappa &\equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \\ \kappa \rho &= \left(\frac{\partial \rho}{\partial P} \right)_T \\ \kappa \rho dP &= d\rho \quad (\text{const } T) \\ \kappa dP &= \frac{d\rho}{\rho} \quad (\text{const } T) \\ \int_{P_1}^{P_2} \kappa dP &= \int_{\rho_1}^{\rho_2} \frac{d\rho}{\rho} \quad (\text{const } T) \end{aligned}$$

Info: $\rho_1 = 0.9881 \text{ g/cm}^3$; (*0.9881 $\frac{\text{g}}{\text{cm}^3}$ from engineering toolbox*)

```
In[*]:=  $\rho_2 = \rho_1 * 1.01;$   

 $\kappa = 44.18 * 10^{-6};$   

 $P_1 = 1;$ 
```

```
In[*]:=  $eq1 = \kappa * (P_2 - P_1) == \text{Log}\left[\frac{\rho_2}{\rho_1}\right];$ 
```

```
In[*]:= Solve[eq1, P2]
```

```
Out[*]:= { { P2  $\rightarrow$  226.222518179 } }
```

```
( * P2=226.223 bar //ANS*)
```

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 degC, how much work is required? At 60 degC, $b=2,700$ bar and $c=0.125 \text{ cm}^3 \text{ g}^{-1}$.

Solution

The key to this problem is to start with the definition of κ given in equation 3.3, and use this equation to solve for the differential volume, and then substitute this into the definition of work in Equation 1.3:

$$\begin{aligned}\kappa &\equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{and} \quad \kappa = \frac{c}{V(P+b)} \\ \therefore \frac{c}{V(P+b)} &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \\ \frac{c}{P+b} &= - \left(\frac{\partial V}{\partial P} \right)_T \\ dV &= -\frac{c \cdot dP}{P+b} \quad (\text{const } T) \\ W &= -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} P \cdot \left(-\frac{c}{P+b} \right) dP = \int_{P_1}^{P_2} P \cdot \left(\frac{c}{P+b} \right) dP\end{aligned}$$

`In[*]:= b = 2700; (*bar*)`

`c = 0.125; (* cm³/g *)`

`(*Solve for absolute work*)`

`In[*]:= W = 1000 * Integrate[c * P / (P + b), {P, 1, 500}]`

`Out[*]:= 5159.05193912`

`(*Units are g * cm³ / bar * bar = bar * cm³ *)`

`W * bar * cm³ * (1 J / (10 bar * cm³)) * (1 kJ / 1000 J) (* //ANS *)`

`Out[*]:= 0.515905193912 kJ`

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.

Solution

$$\begin{aligned}R &= 8.314; \text{ (*J/mol*K*)} \\CV &= 20.785; \text{ (*J/mol*K*)} \\CP &= 29.099; \text{ (*J/mol*K*)} \\T_1 &= 600; \text{ (*K*)} \\P_1 &= 8.; \text{ (*bar*)} \\P_2 &= 1.; \text{ (*bar*)}\end{aligned}$$

Part (a) - Constant volume

$$T_2 = T_1 * \frac{P_2}{P_1} \text{ (*K*)}$$

$$75.$$

$$\Delta U = CV * (T_2 - T_1) \text{ (*J/mol*)} \quad \Delta H = CP * (T_2 - T_1) \text{ (*J/mol*)}$$

$$-10\,912.125$$

$$-15\,276.975$$

$$Q = \Delta U \text{ (*DU=Q+W=Q+0*)}$$

$$-10\,912.125$$

$$W = 0;$$

$$(* \ W = 0 \text{ J/mol*})$$

$$(* \ Q = -10912.1 \text{ J/mol*})$$

$$(* \Delta U = -10912.1 \text{ J/mol*})$$

$$(* \Delta H = -15277.0 \text{ J/mol*}) \text{ (*//ANS part (a)*)}$$

Part (b) - Constant temperature

$$DH = 0;$$

$$DU = 0;$$

$$Q = -R * T1 * \text{Log}\left[\frac{P2}{P1}\right]$$

$$10373.0861865$$

$$W = -Q$$

$$-10373.0861865$$

$$(* W = -10373. \text{ J/mol} *)$$

$$(* Q = 10373. \text{ J/mol} *)$$

$$(* \Delta U = 0 \text{ J/mol} *)$$

$$(* \Delta H = 0 \text{ J/mol} *)$$

$$(* // \text{ANS part (b)} *)$$

Part (c) - Adiabatic

$$Q = 0;$$

$$\gamma = CP / CV;$$

$$W = \frac{R * T1}{\gamma - 1} \left(\left(\frac{P2}{P1} \right)^{(\gamma-1)/\gamma} - 1 \right)$$

$$-5586.44983749$$

$$DU = W$$

$$-5586.44983749$$

$$T2 = T1 * \left(\frac{P2}{P1} \right)^{R/CP}$$

$$331.226854102$$

$$DH = CP * (T2 - T1)$$

$$-7821.02977248$$

$$(* W = -5586. \text{ J/mol} *)$$

$$(* Q = 0. \text{ J/mol} *)$$

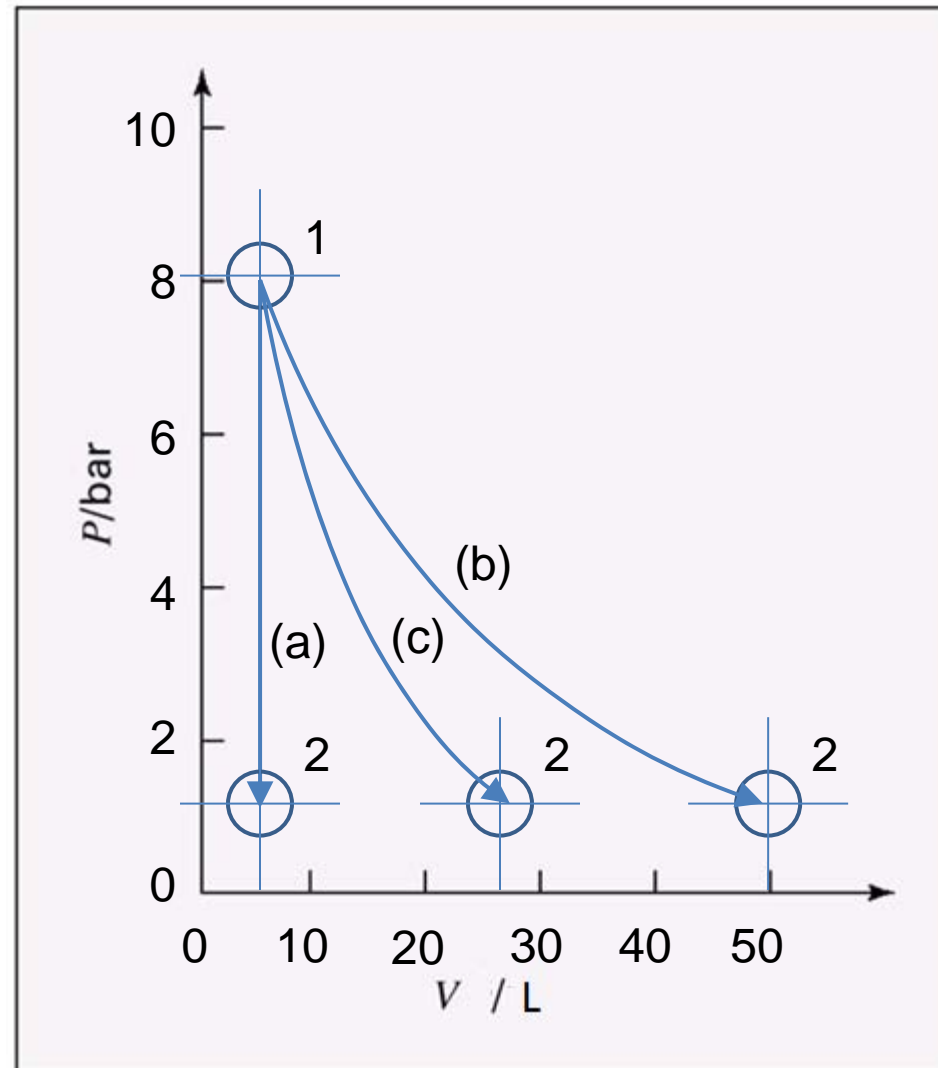
$$(* \Delta U = -5586. \text{ J/mol} *)$$

$$(* \Delta H = -7821. \text{ J/mol} *)$$

$$(* // \text{ANS part (c)} *)$$

Sketches - Parts (a) - (c)

(*Shown on following page*)



Givens:

$$P_1 = 8 \text{ bar}$$

$$T_1 = 600 \text{ K}$$

$$V_1 = 6.24 \text{ L}$$

$$P_2 = 1 \text{ bar}$$

Part (a)

Constant volume

$$V_2 = 6.24 \text{ L}$$

Ideal Gas Equation gives conditions at state 2 for parts (b) and (c)

Part (b)

Isothermal

$$P_2 = 1 \text{ bar}$$

$$T_2 = 600 \text{ K}$$

$$V_2 = 49.92$$

$$P_1 V_1 = P_2 V_2$$

Part (c)

Adiabatic

$$P_2 = 1 \text{ bar}$$

$$T_2 = 331.2 \text{ K}$$

$$V_2 = 27.56 \text{ L}$$

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{R/C_p} = 600 \cdot \left(\frac{1}{8} \right)^{\frac{R}{7R/2}} = 331.2 \text{ K} \quad V_2 = V_1 \left(\frac{P_2}{P_1} \right)^{\frac{-7/2}{5/2}} = 6.24 \cdot \left(\frac{1}{8} \right)^{\frac{-7/2}{5/2}} = 27.56 \text{ L}$$

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:

- (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^t , and ΔH^t for part (a) only. For parts (b) to (e), sketch the path of each process on a single PV diagram.

Solution

```
In[ ]:= Quit[];
```

Common Information for Parts (a)-(e)

(*Since points 1 and 2 are defined on an isotherm in part (a) then $\Delta H=0$ and $\Delta U=0$.*)

(*This can be proven mathematically assuming a closed system:*)

(*Note that the total volume is given, not molar volume.*)

(* $PV^{\text{tot}}=nRT$ *)

(* $\frac{PV^{\text{tot}}}{nT}=\text{constant}$ *)

(*Therefore, $\frac{P_1 V_1^{\text{tot}}}{n_1 T_1} = \frac{P_2 V_2^{\text{tot}}}{n_2 T_2}$ *)

(*Assume $n_1=n_2=n$ for a closed system so n cancels.*)

(*Since $P_1 V_1^{\text{tot}}=P_2 V_2^{\text{tot}}$ (that is, $12 \cdot 1=1 \cdot 12$) then $T_1=T_2$ which means the overall process is isothermal.*)

```
In[ ]:= ΔH = 0; (*//ANS, kJ, parts (a)-(e)*)
```

```
ΔU = 0; (*//ANS, kJ, parts (a)-(e)*)
```

```
P1 = 1.; (*bar*)
```

```
P2 = 12.; (*bar*)
```

```
V1 = 12.; (*m³*)
```

```
V2 = 1.; (*m³*)
```

```
R = 8.314; (*J/mol*K*)
```

```
Cp = (5 / 2) * R;
```

```
Cv = (3 / 2) * R;
```

```
γ = Cp / Cv;
```

(*V, Q, H, and W are total (not molar)*)

Part (a) - Isothermal Compression

$$(*Q=R*T*\text{Log}\left[\frac{V_2}{V_1}\right] \text{ equation 3.20 from L11 slide 6}*)$$

$$(*PV_{\text{tot}}=nRT \rightarrow RT=\frac{PV_{\text{tot}}}{n}*)$$

$$(*nQ=Q_{\text{tot}}=P*V_{\text{tot}}*\text{Log}\left[\frac{V_2}{V_1}\right]*)$$

$$(*RT \text{ is constant so } P_1V_1=P_2V_2*)$$

$$Q = P_1 * V_1 * \text{Log}\left[\frac{V_2}{V_1}\right] \quad (* \text{ bar} * \text{m}^3 *)$$

$$\text{Out}[*]= -29.8188797975$$

$$\text{In}[*]= Q * \text{bar} * \text{m}^3 * \frac{1 \text{ J}}{10^{-5} \text{ bar} * \text{m}^3} * \frac{1 \text{ kJ}}{1000 \text{ J}} \quad (*//\text{ANS part (a)}*)$$

$$\text{Out}[*]= -2981.88797975 \text{ kJ}$$

$$(*\text{Since } \Delta U=0, W=-Q=2981.89 \text{ kJ } //\text{ANS part (a)}*)$$

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

(*STEP 1 - adiabatic compression to 12 bar*)

(*Let Vint be the intermediate volume.*)

$$\text{eqb} = \frac{P_2}{P_1} = \left(\frac{V_1}{V_{\text{int}}} \right)^{C_p/C_v}; \quad (*\text{Un-numbered equation from L11 Slide 9}*)$$

$$V_{\text{int}} = V_1 /. \text{Quiet}[\text{Solve}[\text{eqb}, V_{\text{int}}]] [[1]]$$

Out[]= 2.70192007704

(*STEP 1 - adiabatic compression*)

$$W_1 = \frac{P_2 * V_{\text{int}} - P_1 * V_1}{\gamma - 1} \quad (*\text{bar} * \text{m}^3 *) \quad (*\text{Eq 3.26 L11 slide 10} *)$$

Out[]= 30.6345613867

(*STEP 2 - isobaric cooling at 12 bar*)

$$\text{In[]}:= W_2 = -P_2 * (V_2 - V_{\text{int}}) \quad (*\text{bar} * \text{m}^3 *)$$

Out[]= 20.4230409245

$$\text{In[]}:= W = W_1 + W_2 \quad (*\text{bar} * \text{m}^3 *)$$

Out[]= 51.0576023112

$$\text{In[]}:= W * \text{bar} * \text{m}^3 * \frac{1 \text{ J}}{10^{-5} \text{ bar} * \text{m}^3} * \frac{1 \text{ kJ}}{1000 \text{ J}} \quad (*//\text{ANS part (b)} *)$$

Out[]= 5105.76023112 kJ

(*Since $\Delta U=0$, $Q=-W=-5105.76 \text{ kJ}$ //ANS (part(b) *)

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

(*STEP 1 - adiabatic compression to 1 m³*)

(*Pint is the intermediate pressure*)

$$\text{In[]:= Pint} = P1 * \left(\frac{V1}{V2} \right)^{C_p/C_v} \quad (*\text{un-numbered equation L11 slide}*)$$

Out[]:= 62.897793461

(*from slide 10 in lesson 12 eq 3.26 for work*)

$$W1 = \frac{Pint * V2 - P1 * V1}{\gamma - 1} \quad (*\text{bar} * \text{m}^3*)$$

Out[]:= 76.3466901915

(*STEP 2 - work is zero at const V*)

In[]:= W2 = 0;

$$W = W1 + W2 \quad (*\text{bar} * \text{m}^3*)$$

Out[]:= 76.3466901915

$$\text{In[]:= } W * \text{bar} * \text{m}^3 * \frac{1 \text{ J}}{10^{-5} \text{ bar} * \text{m}^3} * \frac{1 \text{ kJ}}{1000 \text{ J}} \quad (*//\text{ANS part (c)}*)$$

Out[]:= 7634.66901915 kJ

(*Since $\Delta U=0$, $Q=-W=-7634.67 \text{ kJ}$ //ANS part (c)*)

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

(*STEP 1 - isochoric step - work is zero at const V*)

$$\ln[\circ] := W1 = 0;$$

(*STEP 2 - isobaric work at 1 bar is $-P\Delta V$ *)

$$\ln[\circ] := W2 = -P2 * (V2 - V1);$$

$$\ln[\circ] := W = W1 + W2 \quad (*\text{bar} * \text{m}^3 *)$$

$$\text{Out}[\circ] = 132.$$

$$\ln[\circ] := W * \text{bar} * \text{m}^3 * \frac{1 \text{ J}}{10^{-5} \text{ bar} * \text{m}^3} * \frac{1 \text{ kJ}}{1000 \text{ J}} \quad (*//\text{ANS part (d)} *)$$

$$\text{Out}[\circ] = 13200. \text{ kJ}$$

(*Since $\Delta U=0$, $Q=-W=-13200 \text{ kJ}$ //ANS part (d)*)

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

(*STEP 1 - isobaric work at 1 bar is $-P\Delta V$ *)

$$\ln[\circ] := W1 = -P1 * (V2 - V1); \quad (*\text{bar} * \text{m}^3 *)$$

(*STEP 2 - isochoric step - work is zero at const V*)

$$\ln[\circ] := W2 = 0;$$

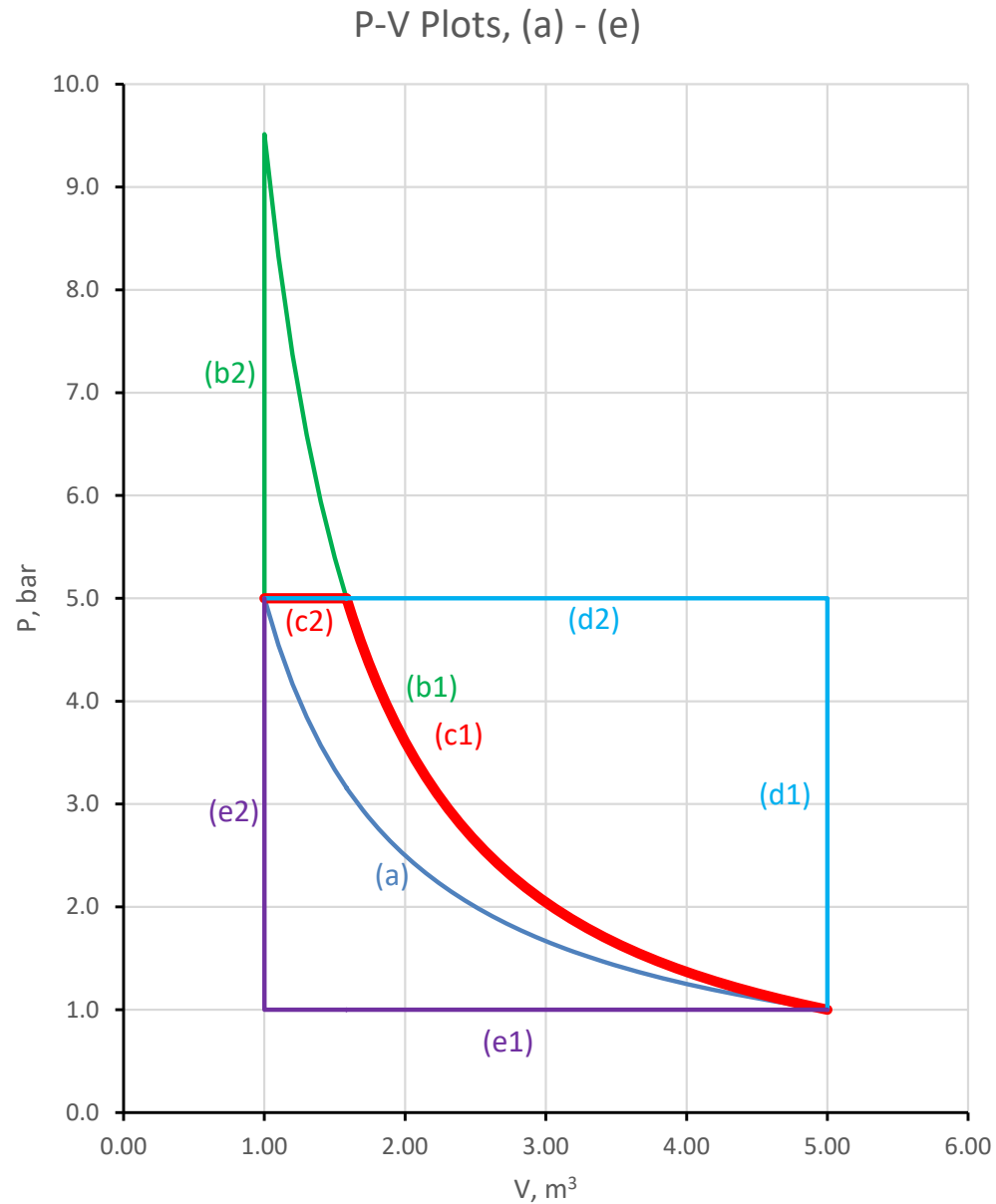
$$W = W1 + W2; \quad (*\text{bar} * \text{m}^3 *)$$

$$\ln[\circ] := W * \text{bar} * \text{m}^3 * \frac{1 \text{ J}}{10^{-5} \text{ bar} * \text{m}^3} * \frac{1 \text{ kJ}}{1000 \text{ J}} \quad (*//\text{ANS} *)$$

$$\text{Out}[\circ] = 1100. \text{ kJ}$$

(*Since $\Delta U=0$, $Q=-W=-1100 \text{ kJ}$ //ANS*)

- (a) isothermal compression
- (b1) adiabatic compression
(b2) cooling at constant pressure
- (c1) adiabatic compression
(c2) cooling at constant volume
- (d1) heating at constant volume
(d2) cooling at constant pressure
- (e1) cooling at constant pressure
(e2) heating at constant volume



actual excel plots

For submission, all five sketches must be on the same PV axes.

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:

$$(a) Z = 1 + \frac{B}{V} + \frac{C}{V^2}$$

$$(b) Z = 1 + B' P + C' P^2$$

$$(c) Z = 1$$

$$(d) Z = 1 + \frac{B}{V}$$

$$\text{where } B' = \frac{B}{RT} \text{ and } C' = \frac{C - B^2}{(RT)^2}$$

Why don't parts (a) and (b) give exactly the same result?

Solution

The key to this problem is understanding the reversible work equation (Equation 1.3) and then understanding how to integrate it. That is,

$$dW = -PdV$$

It is very important to realize that $P=P(V)$, and that whether we are using the ideal gas law or the virial equation, we must substitute the function $P(V)$ into equation 1.3 and integrate from V_1 to V_2 . This means we must also determine V_1 and V_2 .

What follows below for the solution to Part (a) is (1) a determination of V_1 and V_2 , (2) determination of the function for $P(V)$, then (3) integrating Equation 1.2 from V_1 to V_2 .

Part (a)

```
In[ ]:= Quit[ ] ;
```

```
In[ ]:= R = 83.14 (* cm^3*bar / (mol*K) *) ;
```

```
P1 = 1. (* bar *) ;
```

```
P2 = 55. (* bar *) ;
```

```
T = 373.15 (* K *) ;
```

```
B = -242.5 (* cm^3 / mol *) ;
```

```
Unprotect[C] ;
```

```
C = 25200 (* cm^6 / mol^2 *) ;
```

Determination V_1 and V_2 :

```
In[ ]:= eq1 = 
$$\frac{P1 * V1}{R * T} == 1 + \frac{B}{V1} + \frac{C}{V1^2} ;$$

```

```
In[ ]:= Quiet[sol1 = Solve[eq1, V1, Reals]]
```

```
Out[ ]:= { {V1 -> 30780.097043} }
```


$$V1 = V1 /. \text{sol1}[[1]] \text{ (*units are } \frac{\text{cm}^3}{\text{mol}} \text{ *)}$$

Out[]:= 30780.097043

$$\text{In[]:= eq2} = \frac{P2 * V2}{R * T} == 1 + \frac{B}{V2} + \frac{C}{V2^2};$$

In[]:= Quiet[sol2 = Solve[eq2, V2, Reals]]

Out[]:= {{V2 → 241.333143561}}

$$\text{In[]:= V2} = V2 /. \text{sol2}[[1]] \text{ (*units are } \frac{\text{cm}^3}{\text{mol}} \text{ *)}$$

Out[]:= 241.333143561

Determination the function P(V):

$$\text{In[]:= P[V_]} = \left(1 + \frac{B}{V} + \frac{C}{V^2}\right) * \frac{R * T}{V}; \text{ (*bar*)}$$

Integrate equation 1.3:

$$\text{In[]:= W} = - \int_{V1}^{V2} (P[V]) \, dV \quad \left(* \frac{\text{bar} * \text{cm}^3}{\text{mol}} *\right)$$

Out[]:= 126198.643583

(*Put dimensions of work into kJ:*)

$$\text{In[]:= 126199.} * \frac{\text{bar} * \text{cm}^3}{\text{mol}} * \frac{10^5 \text{ Pa}}{\text{bar}} * \frac{\frac{1 \text{ N}}{\text{m}^2}}{\text{Pa}} * \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 * \frac{1 \text{ J}}{1 \text{ N} * \text{ m}} * \frac{1 \text{ kJ}}{1000 \text{ J}} * 1 \text{ mol}$$

Out[]:= 12.6199 kJ

(* //ANS*)

Part (b)

The solution for Part (b) is a little different. In this case, we are asked to use the virial equation in the form of a power series expansion in P. In this equation (given above), V is easy to isolate, so the strategy is to isolate it, then evaluate dV. This produces an expression in terms of dP. Substitute the new dV into equation 1.3, and integrate with respect to pressure (instead of volume). This means the limits of integration are P1 and P2, not V1 and V2 as in Part (a).

What follows below the solution to Part (b) is (1) a determination of V(P), then (2) determination work using Equation 1.3 after substituting in dV.

Determine the function V(P):

```

In[ ]:= Bprime =  $\frac{B}{R * T}$  ; (*Eq 3-35a slide 13*)

Cprime =  $\frac{C - B^2}{(R * T)^2}$  ; (*Eq 3-35b*)

(*Solve eq 3.34 for V in terms of P*)

In[ ]:= V[P_] =  $\left(1 + Bprime * P + Cprime * P^2\right) * \frac{R * T}{P}$  ;

```

Integrate equation 1.3 (dW=-PdV) with respect to P after substituting dV=V'dP:

```

In[ ]:= W = -  $\int_{P1}^{P2} P * V' [P] dP$ 

Out[ ]:= 125960.132515

In[ ]:=  $125960. * \frac{\text{bar} * \text{cm}^3}{\text{mol}} * \frac{10^5 \text{ Pa}}{\text{bar}} * \frac{\frac{1 \text{ N}}{\text{m}^2}}{\text{Pa}} * \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 * \frac{1 \text{ J}}{1 \text{ N} * \text{m}} * \frac{1 \text{ kJ}}{1000 \text{ J}} * 1 \text{ mol}$ 

Out[ ]:= 12.596 kJ

(* /ANS*)

```

Part (c)

Proceed as in Part (a) - find V1 and V2, write P(V), substitute into equation 1.3, and integrate:

```

In[ ]:= Clear[V1, V2] ;

In[ ]:= eq1 =  $\frac{P1 * V1}{n * R * T} == 1$  ;

In[ ]:= Quiet[sol1 = Solve[eq1, V1]]

Out[ ]:= { {V1 -> 31023.691 n} }

In[ ]:= V1 = V1 /. sol1[[1]]

Out[ ]:= 31023.691 n

In[ ]:= eq2 =  $\frac{P2 * V2}{n * R * T} == 1$  ;

In[ ]:= Quiet[sol2 = Solve[eq2, V2]]

Out[ ]:= { {V2 -> 564.067109091 n} }

In[ ]:= V2 = V2 /. sol2[[1]]

Out[ ]:= 564.067109091 n

In[ ]:= Pideal[V_] =  $\frac{R * T}{V}$  ;

```

$$\text{In}[*]:= W = - \int_{V_1}^{V_2} P_{\text{ideal}}[V] \, dV$$

$$\text{Out}[*]:= 124322.266473$$

$$\text{In}[*]:= 124322. * \frac{\text{bar} * \text{cm}^3}{\text{mol}} * \frac{10^5 \text{ Pa}}{\text{bar}} * \frac{\frac{1 \text{ N}}{\text{m}^2}}{\text{Pa}} * \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 * \frac{1 \text{ J}}{1 \text{ N} * \text{m}} * \frac{1 \text{ kJ}}{1000 \text{ J}} * 1 \text{ mol}$$

$$\text{Out}[*]:= 12.4322 \text{ kJ}$$

(*/ANS*)

The work equation can also be integrated with respect to P/ as in part (b), resulting in exactly the same answer:

$$\text{In}[*]:= V[P_] = \frac{R * T}{P};$$

$$\text{In}[*]:= W = - \int_{P_1}^{P_2} P * V'[P] \, dP$$

$$\text{Out}[*]:= 124322.266473$$

Part (d)

This problem is a little tricky because the equation is quadratic and there are no real roots for V2. Essentially, the problem cannot be solved as posed. We can come close, though. To get a reasonable approximation, use the values of V1 and V2 determined in Part (a).

$$\text{In}[*]:= V1 = 30780.1;$$

$$V2 = 241.33;$$

$$\text{In}[*]:= P[V_] = \left(1 + \frac{B}{V} \right) * \frac{R * T}{V}; (*bar*)$$

$$\text{In}[*]:= W = - \int_{V_1}^{V_2} P[V] \, dV$$

$$\text{Out}[*]:= 119487.395271$$

$$\text{In}[*]:= 119487. * \frac{\text{bar} * \text{cm}^3}{\text{mol}} * \frac{10^5 \text{ Pa}}{\text{bar}} * \frac{\frac{1 \text{ N}}{\text{m}^2}}{\text{Pa}} * \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 * \frac{1 \text{ J}}{1 \text{ N} * \text{m}} * \frac{1 \text{ kJ}}{1000 \text{ J}} * 1 \text{ mol}$$

$$\text{Out}[*]:= 11.9487 \text{ kJ}$$

(*/ANS*)