# Problem Set 4 - Solutions

#### 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  $\beta$ -maiasmone. Examine the claim using the Gibbs phase rule and provide a plausible explanation for your results.

#### Solution

The report is incorrect because it violates 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 in 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

#### Problem 3.6

Express the volume expansivity ( $\beta$ ) and isothermal compressibility ( $\kappa$ ) 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  $\kappa$  is independent of P.

# Part 1 - Express $\beta$ and $\kappa$ as functions of $\rho$ and its partial derivatives

Express  $\beta$  and  $\kappa$  as functions of density and its partial derivatives. The key to t his 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).

From class, for V=V(T,P):

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\frac{dV}{V} = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P dT + \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T dP$$
if  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  and  $\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ , then

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

Solution:= - Repeat the derivation using  $\rho = \rho(T,P)$ :

$$d\rho = \left(\frac{\partial \rho}{\partial T}\right)_P dT + \left(\frac{\partial \rho}{\partial P}\right)_T dP$$

$$\frac{\mathrm{d}\rho}{\rho} = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_P \mathrm{d}T + \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T \mathrm{d}P$$

if 
$$\beta = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_P$$
 and  $\kappa = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T$ , then

$$\frac{\mathrm{d}\rho}{\rho} = -\beta \mathrm{dT} + \kappa \mathrm{dP}$$

#### Comments:

Cadets tend to put the wrong signs on  $\beta$  and  $\kappa$ .

 $\beta$  is a positive quantity because in the original derivation,  $\beta \equiv (\partial V/\partial T)_P/V$ . Since molar volume is always positive and molar volume increases as temperature increases, the derivative is also always positive.

To be consistent with this in the density form, we must use a negative sign in front of  $\partial \rho/\partial T$ , because as temperature goes up, density goes down, making the derivative  $\partial \rho/\partial T$  negative.

It is desirable to keep  $\beta$  the same since the property itself does not change. The negative sign compensates for the negative derivative.

Likewise, when derived from density,  $\kappa$  uses a positive sign in front of the derivative because density increases as pressure increases, so  $(\partial \rho / \partial P)_T$  is positive.

In the original derivation from molar volume V, we used a negative sign for  $\kappa$  because  $(\partial V/\partial P)_T$  is negative. That is, molar volume decreases as pressure increases.

# Part 2 - To what pressure must water be compressed?

Cadets are asked to calculate the pressure required to change the density by 1% at 50 °C. That is, change the pressure at constant T and calculate the density response. This relationship is described by  $\kappa$ , so rearrange and integrate as shown:

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

Multiply both sides by  $\rho$ :

$$\kappa \rho = \left(\frac{\partial \rho}{\partial P}\right)_T$$

Multiply both sides by dP and re-write as a differential equation (at constant T):

$$\kappa \rho dP = d\rho$$

Separate variables:

$$\kappa dP = \frac{\partial \rho}{\rho}$$

Integrate both sides of the equation:

$$\int_{P_1}^{P_2} \kappa \, dP = \int_{\rho_1}^{\rho_2} \frac{1}{\rho} \, d\rho$$

Solve:

```
\rho1 = 0.9881; (*0.9881 g/cm<sup>3</sup> from engineering toolbox*)
          \rho2 = \rho1 * 1.01;
          \kappa = 44.18 * 10^{-6};
          P1 = 1;
 In[•]:= eq1 = \kappa * (P2 - P1) = Log\left[\frac{\rho^2}{\rho^2}\right];
 In[ • ]:= Solve[eq1, P2]
Out[ • ]=
           \{ \{ P2 \rightarrow 226.2225 \} \}
```

The water must be compressed to 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 °C, how much work is required? At 60 °C, b=2,700 bar and c=0.125  $cm^3 q^{-1}$ .

#### Solution

Start with the two definitions of  $\kappa$ :

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

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

Equate the two definitions:

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

Multiply both sides by V:

$$\frac{c}{(P+b)} = -\left(\frac{\partial V}{\partial P}\right)_T$$

Multiply both sides by dP (assuming constant T):

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

Write equation 1.3, substitute the new equation for dV, and integrate:

$$W = -\int_{V_1}^{V_2} P \, dl \, V = \int_{P_1}^{P_2} \left( \frac{c \, P}{P + b} \right) \, dl \, P$$

$$In[\circ] := b = 2700; \, (*bar*)$$

$$c = 0.125; \, (*\frac{cm^3}{g}*)$$

$$(*Solve for absolute work*)$$

$$In[\circ] := W = 1000 * \int_1^{500} \frac{c * P}{P + b} \, dl \, P$$

$$Out[\circ] = 5159.052$$

(\*Units are bar\*cm³ since  $g*\frac{\frac{cm^3}{8}*bar}{bar}*bar=bar*cm³*)$ 

Convert units to kJ:

W \* bar \* cm<sup>3</sup> \* 
$$\frac{1 \text{ J}}{10 \text{ bar * cm}^3}$$
 \*  $\frac{1 \text{ kJ}}{1000 \text{ J}}$  (\*//ANS\*)

Out[0]=

0.515 905 2 kJ

The required work is 0.515905 kJ. //ANS

### 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 bar and  $T_1$  = 600 K to  $P_2$  = 1 bar by each of the following paths:

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

Assuming mechanical reversibility, calculate W, Q,  $\Delta$ U, and  $\Delta$ H for each process. Sketch each path on a single PV diagram.

#### Common Information

# Part (a) - Constant Volume

# Part (b) - Constant Temperature

```
DH = 0;
DU = 0;
Q = -R * T1 * Log \left[ \frac{P2}{P1} \right]
10373.09
W = -Q
-10373.09
(* W = -10373. J/mol*)
(* Q = 10373. J/mol*)
(*\Delta U = 0 \text{ J/mol*})
(*\Delta H = 0 J/mol*)
(*//ANS part (b)*)
```

### Part (c) - Adiabatic

$$Q = 0;$$
 $\gamma = CP / CV;$ 

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

$$-5586.45$$

$$DU = W$$

$$-5586.45$$

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

$$331.2269$$

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

$$-7821.03$$

$$(* W = -5586. J/mol*)$$

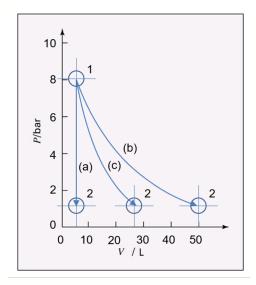
$$(* Q = 0. J/mol*)$$

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

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

$$(* //ANS part (c) *)$$

# Sketches for parts (a) to (c)



V2 Calculations for sketch:

$$In[\circ]:= \text{ (*constant volume V1=V2*)}$$

$$\text{V2(*or V1*)} = \frac{1 \text{ mol} * .08313 \frac{bar*L}{mol*K} * 600 \text{ K}}{8 \text{ bar}}$$

$$Out[\circ]=$$

6.23475 L

$$In[\circ]:= (*contant temperature*)$$

$$V2 = \frac{1 \text{ mol} * .08313 \frac{bar*L}{mol*K} * 600 \text{ K}}{1 \text{ bar}}$$

$$Out[\circ]:= 49.878 \text{ L}$$

$$(*Adiabatic*)$$

$$(*P1*V1^{\gamma}=P2*V2^{\gamma}**)$$

$$V2 = \frac{1.4}{\sqrt[4]{P1*V1^{1.4}}} // \text{ PowerExpand}$$

$$Out[\circ]:= 27.53489 \text{ L}^{1}.$$

#### Problem 3.21

An ideal gas,  $C_P = (5/2) R$  and  $C_V = (3/2) R$ , is changed from  $P_1 = 1$  bar and  $V_1^t = 12 m^3$  to  $P_2 = 12$  bar and  $V_2^t = 1 m^3$  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,  $\Delta U^t$ , and  $\Delta H^t$  for each of these processes, and sketch the paths of all processes on a single PV diagram.

# Common Information for Parts (a) to (e)

Since points 1 and 2 are defined on an isotherm in part (a) then  $\Delta H=0$  and  $\Delta U=0$ . These are the same initial and final points for all five parts of the problem. So  $\Delta H=0$  and  $\Delta U=0$  for parts (a) through (e). Also, carefully note that V, Q,  $\Delta$ H,  $\Delta$ U, and W are total (not molar).

```
\Delta H = 0; (*//ANS, parts (a) - (e) *)
\Delta U = 0; (*//ANS, parts (a) - (e) *)
P1 = 1.; (*bar*)
P2 = 12.; (*bar*)
V1 = 12.; (*m<sup>3</sup>*)
V2 = 1.; (*m^3*)
R = 8.314; (*J/mol*K*)
C_p = (5/2) * R;
C_V = (3/2) * R;
\gamma = C_P / C_V;
```

51.0576

## Part (a) - Isothermal compression

```
ln[\cdot]:= W*bar*m^3*\frac{1J}{10^{-5}bar*m^3}*\frac{1kJ}{1000J} (*//ANS part (b)*)
Out[0]=
        5105.76 kJ
        (*\Delta H = \Delta U = 0, and 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 m<sup>3</sup>*)
        (*Pint is the intermediate pressure*)
 In[\cdot]:= Pint = P1 * \left(\frac{V1}{V2}\right)^{C_P/C_V} (*un-numbered equation L11 slide*)
Out[0]=
        62.89779
 In[*]:= (*from slide 10 in lesson 12 eq 3.26 for work*)
        W1 = \frac{Pint * V2 - P1 * V1}{\gamma - 1} \quad (*bar*m^3*)
Out[ • ]=
        76.34669
 (*STEP 2 - work is zero at const V*)
 In[ \circ ] := W2 = 0;
        W = W1 + W2 (*bar*m^3*)
Out[•]=
        76.34669
 ln[\cdot]:= W*bar*m^3*\frac{1J}{10^{-5}bar*m^3}*\frac{1kJ}{1000J} (*//ANS part (c)*)
Out[0]=
        7634.669 kJ
        (*\DeltaH=\DeltaU=0, and since \DeltaU=0, Q=-W=-7634.67 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*)
 In[ • ]:= W1 = 0;
  (*STEP 2 - isobaric work at 1 bar is -P△V*)
 ln[ \circ ] := W2 = -P2 * (V2 - V1);
 In[ \circ ] := W = W1 + W2 (*bar*m^3*)
```

Out[ • ]=

132.

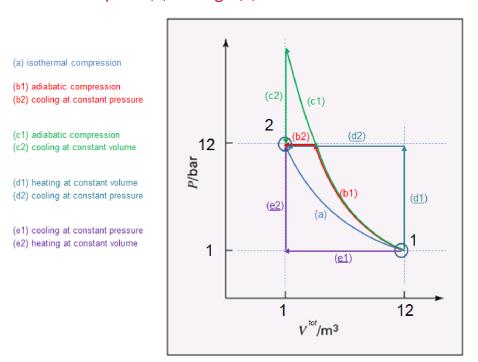
$$In[\circ]:= \ \ \, \text{W}* \, \text{bar}* \, \text{m}^3 * \frac{1}{10^{-5}} \, \text{bar}* \, \text{m}^3 * \frac{1}{1000} \, \text{J} \ \ \, (*//ANS \, \, \text{part} \, \, (d)*)$$

$$Out[\circ]:= \\ 13\,200. \, \text{kJ}$$

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

# Part (e) - Cooling at Constant Pressure followed by heating at constant volume

## Sketches for parts (a) through (e)



### Problem 3.42

For methyl chloride at 100 °C, 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 °C.

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

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

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

(c) 
$$Z = 1$$

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

#### **Solution Comments**

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 consistent values  $V_1$  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 1.3 from  $V_1$  to  $V_2$ .

### Part (a)

In[o]:= R = 83.14 (\* 
$$\frac{\text{cm}^3 * \text{bar}}{\text{mol} * \text{K}} *$$
);  
P1 = 1. (\*bar\*);  
P2 = 55. (\*bar\*);  
T = 373.15 (\*K\*);  
B = -242.5 (\*  $\frac{\text{cm}^3}{\text{mol}} *$ );  
C = 25200 (\*  $\frac{\text{cm}^6}{\text{mol}^2} *$ );

(1) Determination  $V_1$  and  $V_2$ :

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

V1 = SolveValues[eq1, V, Reals] [1] (\*units are 
$$\frac{cm^3}{mol}$$
\*)

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

V2 = SolveValues[eq2, V, Reals] [1] (\*units are  $\frac{\text{cm}^3}{\text{mol}}$ \*)

Out[ • ]= 241.3331

(2) Determination of the function P(V):

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

(3) Integration of equation 1.3:

$$W = -\int_{V1}^{V2} (P[V]) dV \quad (*units are bar* \frac{cm^3}{mol}*)$$

Out[0]=

126198.6

(\*Put dimensions of work into kJ:\*)

$$ln[*]:=$$
 126199. \*  $\frac{bar * cm^3}{mol} * \frac{1 J}{10 bar * cm^3} * \frac{1 kJ}{1000 J} * 1 mol$ 

Out[ • ]=

12.6199 kJ

The reversible work is 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 ore 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.

(1) Determine the function V(P):

Bprime = 
$$\frac{B}{R * T}$$
; (\*given; units are bar<sup>-1</sup>\*)

Cprime = 
$$\frac{c - B^2}{(R * T)^2}$$
; (\*given; units are bar<sup>-2</sup>\*)

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

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

$$ln[\cdot]:= W = -\int_{P1}^{P2} P \star V'[P] dP$$

Out[•]=

125 960.1

$$ln[*]:=$$
 125 960. \*  $\frac{bar * cm^3}{mol}$  \*  $\frac{1}{10 bar * cm^3}$  \*  $\frac{1 kJ}{1000 J}$  \* 1 mol Out[\*]=

The reversible work is 12.596 kJ. //ANS

### Part (c)

Proceed as in Part (a) - find  $V_1$  and  $V_2$ , write P(V), substitute into equation 1.3, and integrate:

$$In[*] := \text{Clear[V1, V2];}$$

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

$$In[*] := \text{Quiet[sol1} = \text{Solve[eq1, V1]]}$$

$$Out[*] := \{V1 \to 31023.69 \text{ n}\}\}$$

$$In[*] := \text{V1} = \text{V1 / . sol1[[1]]}$$

$$Out[*] := 31023.69 \text{ n}$$

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

$$In[*] := \text{Quiet[sol2} = \text{Solve[eq2, V2]]}$$

$$Out[*] := \{V2 \to 564.0671 \text{ n}\}\}$$

$$In[*] := \text{V2} = \text{V2 / . sol2[[1]]}$$

$$Out[*] := 564.0671 \text{ n}$$

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

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

$$In[*] := \text{V2} = \text{V2} =$$

The reversible work is 12.4322 kJ. //ANS

12.4322 kJ

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

$$In[\cdot]:=V[P_{-}]=\frac{R*T}{P};$$
 $In[\cdot]:=W=-\int_{P_{1}}^{P_{2}}P*V'[P] dP$ 
 $Out[\cdot]=$ 
 $124\,322.3$ 

### Part (d)

This problem is a little tricky because the equation is quadratic and there are no real roots for  $V_2$ . Essentially, the problem cannot be solved as posed. We can come close, though, using a fix. To get a reasonable approximation, use the values of  $V_1$  and  $V_2$  determined in Part (a).

In[
$$\circ$$
]:= V1 = 30 780.1;  
V2 = 241.33;  
In[ $\circ$ ]:= P[V\_] =  $\left(1 + \frac{B}{V}\right) * \frac{R * T}{V}$ ; (\*bar\*)  
In[ $\circ$ ]:= W =  $-\int_{V1}^{V2}$  P[V] dlV  
Out[ $\circ$ ]:= 119 487.4  
In[ $\circ$ ]:= 119 487. \*  $\frac{bar * cm^3}{mol} * \frac{1}{10} \frac{1}{bar * cm^3} * \frac{1}{10000} \frac{1}{10000} * 1 mol$ 
Out[ $\circ$ ]:= 11.9487 kJ

The reversible work is 11.9487 kJ. //ANS