

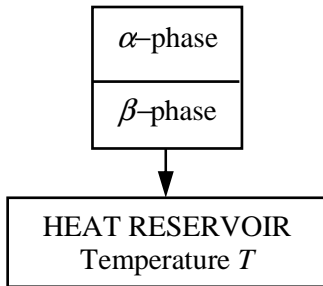
Module 3A5 : Thermodynamics and Power Generation

THERMODYNAMICS

Solutions to Examples Paper 2

(J.B. Young, October 2007)

1.

Total volume of system is $V = V_\alpha + V_\beta$ System enclosed in rigid container so $dV = 0$.At equilibrium, $T_\alpha = T_\beta = T$ and $p_\alpha = p_\beta = p$.Heat reservoir maintains T constant so $dT = 0$.

- (a) From
- $f_i = u_i - Ts_i$
- and
- $Tds_i = du_i + pdv_i$
- (and also
- $dT = 0$
-):

$$df_i = du_i - Tds_i - s_i dT = -pdv_i - s_i dT = -pdv_i \quad (1)$$

If there is a small transfer of mass from one phase to the other, T and V stay the same but V_α and V_β (and hence the pressure) all change a little. The specific volumes v_i also change (because they depend on T and p via the equation of state for each phase).

- (b) The Helmholtz function of the whole system is
- $F = m_\alpha f_\alpha + m_\beta f_\beta$
- . With
- T
- and
- V
- constant, equilibrium corresponds to a minimum value of
- F
- so,

$$dF = m_\alpha df_\alpha + f_\alpha dm_\alpha + m_\beta df_\beta + f_\beta dm_\beta = 0$$

Using eq. (1),

$$dF = -pm_\alpha dv_\alpha + f_\alpha dm_\alpha - pm_\beta dv_\beta + f_\beta dm_\beta = 0 \quad (2)$$

The total volume $V = m_\alpha v_\alpha + m_\beta v_\beta$ is constant. Hence,

$$dV = m_\alpha dv_\alpha + v_\alpha dm_\alpha + m_\beta dv_\beta + v_\beta dm_\beta = 0 \quad (3)$$

Multiplying eq. (3) by p and adding to eq. (2) gives,

$$dF = (f_\alpha + pv_\alpha)dm_\alpha + (f_\beta + pv_\beta)dm_\beta = 0$$

Noting that $f_i + pv_i = g_i = \mu_i$ we have,

$$dF = \mu_\alpha dm_\alpha + \mu_\beta dm_\beta = 0$$

For an interphase transfer of mass keeping the total mass constant, $dm_\beta = -dm_\alpha$. Thus,

$$dF = (\mu_\alpha - \mu_\beta)dm_\alpha = 0$$

There is no restriction on dm_α so $\mu_\alpha = \mu_\beta$ at equilibrium.

2. The Clausius-Clapeyron equation is,

$$\frac{dp_s}{dT} = \frac{h_{fg}}{v_{fg}T}$$

We make the approximations $v_g \gg v_f$ and $p_s v_g = RT$ which are reasonable if the temperature is much less than the critical temperature. Hence,

$$\left(\frac{dp_s}{dT}\right) \cong \frac{p_s h_{fg}}{RT^2}$$

Integrating between states 1 and 2 on the saturation line assuming h_{fg} is constant gives,

$$\ln\left(\frac{p_{s2}}{p_{s1}}\right) \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

For saturated steam with $T_1 = 40^\circ\text{C} = 313.15\text{ K}$ and $T_2 = 100^\circ\text{C} = 373.15\text{ K}$, taking $h_{fg} = 2333.0\text{ kJ/kg}$ at 70°C and $R = 8.3143/18 = 0.462\text{ kJ/kg K}$,

$$\frac{p_{s2}}{p_{s1}} \cong 13.37 \quad (\text{Exact value is } 13.73 \text{ from Steam Tables in the Data Book})$$

3(a) From $f = u - Ts$ and $Tds = du + pdv$, we have,

$$df = du - Tds - sdT = -pdv - sdT$$

Hence,

$$\begin{aligned}\left(\frac{\partial f}{\partial v}\right)_T &= -p & \left(\frac{\partial f}{\partial T}\right)_v &= -s \\ \frac{\partial^2 f}{\partial v \partial T} &= -\left(\frac{\partial p}{\partial T}\right)_v & \frac{\partial^2 f}{\partial T \partial v} &= -\left(\frac{\partial s}{\partial v}\right)_T \\ \left(\frac{\partial p}{\partial T}\right)_v &= \left(\frac{\partial s}{\partial v}\right)_T\end{aligned}$$

(b) Applying $du = -pdv + Tds$ to changes along an isothermal,

$$\left(\frac{\partial u}{\partial v}\right)_T = -p + T\left(\frac{\partial s}{\partial v}\right)_T$$

Using the Maxwell relation,

$$\left(\frac{\partial u}{\partial v}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_v$$

This is a completely general thermodynamic relation which relates the volume dependence of the internal energy to the p - v - T equation of state. For an ideal gas, we have $p v = RT$ and hence,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$$

Thus,

$$\left(\frac{\partial u}{\partial v}\right)_T = -p + \frac{RT}{v} = 0$$

So $u = u(T)$ for an ideal gas. By definition,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

and hence $c_v = c_v(T)$ for an ideal gas. A special case of this is $c_v = \text{constant}$.

$$4(a) \quad f = c(T-T_0) - cT \ln\left(\frac{T}{T_0}\right) - RT \ln\left(\frac{v-b}{v_0-b}\right) - a\left(\frac{1}{v} - \frac{1}{v_0}\right)$$

From the differential relationship $df = -pdv - sdT$ we have,

$$-p = \left(\frac{\partial f}{\partial v}\right)_T = \frac{-RT}{(v-b)} + \frac{a}{v^2}$$

This is the van der Waals equation,

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT$$

(b) The specific entropy is given by,

$$-s = \left(\frac{\partial f}{\partial T}\right)_v = c - c \ln\left(\frac{T}{T_0}\right) - \frac{cT}{T} - R \ln\left(\frac{v-b}{v_0-b}\right)$$

Hence,

$$s = c \ln\left(\frac{T}{T_0}\right) + R \ln\left(\frac{v-b}{v_0-b}\right)$$

The specific internal energy is given by,

$$u = f + Ts = c(T-T_0) - a\left(\frac{1}{v} - \frac{1}{v_0}\right)$$

The specific heat capacity at constant volume is given by,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = c$$

For a van der Waals fluid, c_v is a constant but u varies with v as well as T . Evidently, $u = 0$ and $s = 0$ when $T = T_0$ and $v = v_0$. Hence (T_0, v_0) is the arbitrary datum state for u and s . It then follows that $f = 0$ at (T_0, v_0) .

(c) By definition $h = u + pv$. Hence,

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = \left(\frac{\partial u}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p = c + \frac{a}{v^2}\left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p$$

We now know that $c = c_v$ and so,

$$c_p - c_v = \left(p + \frac{a}{v^2}\right)\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT}{(v-b)}\left(\frac{\partial v}{\partial T}\right)_p$$

We can get $(\partial v/\partial T)_p$ from the p - v - T equation of state but the algebra is rather messy and the result is not very informative. However, note that $c_p - c_v \neq R$ for a van der Waals fluid.

5. The van der Waals equation of state is,

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v}-b) = \bar{R}T$$

Differentiating to find the critical point conditions:

$$\left(\frac{\partial p}{\partial \bar{v}}\right)_T = -\frac{\bar{R}T}{(\bar{v}-b)^2} + \frac{2a}{\bar{v}^3} = 0 \quad \text{at } T = T_C, \quad \bar{v} = \bar{v}_C.$$

$$\left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T = \frac{2\bar{R}T}{(\bar{v}-b)^3} - \frac{6a}{\bar{v}^4} = 0 \quad \text{at } T = T_C, \quad \bar{v} = \bar{v}_C.$$

Solving these equations simultaneously gives,

$$a = \frac{9\bar{v}_C\bar{R}T_C}{8} \quad b = \frac{\bar{v}_C}{3}$$

According to the van der Waals equation, the ‘excluded’ molar volume is one third of the molar volume at the critical point. Substituting for a and b in the equation of state and setting $p=p_C$, $T=T_C$ and $\bar{v}=\bar{v}_C$ gives the value of the compressibility factor at the critical point,

$$Z_C = \frac{p_C\bar{v}_C}{\bar{R}T_C} = \frac{3}{8}$$

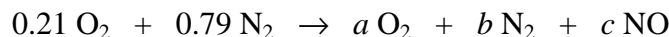
Substituting the definitions of the reduced pressure, temperature and volume in the equation of state gives,

$$\left(p_R p_C + \frac{a}{V_R^2 \bar{v}_C^2}\right)(V_R \bar{v}_C - b) = \bar{R}T_R T_C$$

Introducing the expressions for a , b and Z_C then gives the ‘universal’ form,

$$\left(p_R + \frac{3}{V_R^2}\right)(3V_R - 1) = 8T_R$$

6(a) The chemical equation is,



(b) Conservation of atomic O $\rightarrow 2a + c = 2 \times 0.21 = 0.42$ (i)

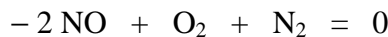
Conservation of atomic N $\rightarrow 2b + c = 2 \times 0.79 = 1.58$ (ii)

No. of moles of products $\rightarrow a + b + c = n$

Partial pressures :

$$p_{\text{O}_2} = \frac{a}{n} p \quad p_{\text{N}_2} = \frac{b}{n} p \quad p_{\text{NO}} = \frac{c}{n} p$$

Reaction 4 in the Data Book is,



The equilibrium constant is therefore defined by,

$$K_p(T) = \left(\frac{p_{\text{NO}}}{p_0} \right)^{-2} \left(\frac{p_{\text{O}_2}}{p_0} \right)^{+1} \left(\frac{p_{\text{N}_2}}{p_0} \right)^{+1}$$

where $p_0 = 1$ bar. From the Data Book at 2000 K, $\ln(K_p) = 7.824$, giving $K_p = 2599.9$. Hence,

$$2499.9 = \frac{(a/n)(b/n)}{(c/n)^2} = \frac{ab}{c^2} \quad \text{(iii)}$$

We now have three equations for the three unknowns a , b and c . Substituting (i) and (ii) into (iii) gives,

$$2499.9c^2 = \frac{(0.42-c)(1.58-c)}{2} \frac{1.58-c}{2}$$

Collecting terms,

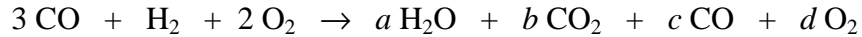
$$9998.6c^2 + 2c - 0.6636 = 0$$

The solution is $c = 0.0080$. From (i) and (ii) $a = 0.2060$, $b = 0.7860$. Also, $n = 1.0$.

The mole fractions are, $X_{\text{NO}} = 0.0080$, $X_{\text{O}_2} = 0.2060$, $X_{\text{N}_2} = 0.7860$

(c) If the pressure were raised to 5 bar, the mole fractions would remain the same. This is because, in the reaction $\text{O}_2 + \text{N}_2 \leftrightarrow 2\text{NO}$, the total number of moles does not change. Hence, there is no effect of pressure.

7(a) With stoichiometric O₂, the chemical reaction is,



$$\text{Conservation of atomic H} \rightarrow 1 = a \quad (\text{i})$$

$$\text{Conservation of atomic C} \rightarrow 3 = b + c \quad (\text{ii})$$

$$\text{Conservation of atomic O} \rightarrow 7 = a + 2b + c + 2d \quad (\text{iii})$$

$$\text{No. of moles of products} \rightarrow n = a + b + c + d \quad (\text{iv})$$

If the pressure after combustion is p_2 , the partial pressures are :

$$p_{\text{H}_2\text{O}} = \frac{a}{n} p_2 \quad p_{\text{CO}_2} = \frac{b}{n} p_2 \quad p_{\text{CO}} = \frac{c}{n} p_2 \quad p_{\text{O}_2} = \frac{d}{n} p_2$$

Reaction 7 in the Data Book is : $-\text{CO} - \frac{1}{2} \text{O}_2 + \text{CO}_2 = 0$

The equilibrium constant is therefore given by,

$$K_{p7}(T_2) = \left(\frac{p_{\text{CO}}}{p_0} \right)^{-1} \left(\frac{p_{\text{O}_2}}{p_0} \right)^{-1/2} \left(\frac{p_{\text{CO}_2}}{p_0} \right)^{+1}$$

where $p_0 = 1$ bar (standard pressure) and $T_2 = 2600$ K. From the Data Book,

$$\ln(K_{p7}) = 2.800 \rightarrow K_{p7} = 16.445$$

Hence,

$$16.445 = \frac{(b/n)}{(c/n)(d/n)^{0.5} (p_2/p_0)^{0.5}}$$

The combustion is at constant volume. If all species behave as ideal gases,

$$p_1 V = 6 \bar{R} T_1$$

$$p_2 V = n \bar{R} T_2$$

where $p_1 = 2$ bar and $T_1 = 400$ K are the initial pressure and temperature. Hence,

$$\frac{p_2}{p_0} = \frac{n}{6} \frac{p_1}{p_0} \frac{T_2}{T_1} = \frac{2 \times 2600}{6 \times 400} n = 2.1667n$$

Substituting into the equilibrium equation we obtain,

$$\frac{b}{c d^{0.5}} = 16.445 \times (2.1667)^{0.5} = 24.207 \quad (\text{v})$$

It is just chance that n cancels out. We now have 5 equations for the 5 unknowns a , b , c , d and n . The solution must be obtained iteratively and one strategy is as follows :

Combine (i), (ii) and (iii) to give,

$$c = 2d$$

$$b = 3 - 2d$$

Substitute for b and c in (v) to give,

$$48.414d^{3/2} = 3 - 2d$$

Starting with a value of $d = 0$ on the RHS, the iteration proceeds as follows :

$$d = 0.0 \rightarrow d = 0.156591 \rightarrow d = 0.145494 \rightarrow d = 0.146294 \rightarrow d = 0.146236 \\ \rightarrow d = 0.146241 \rightarrow d = 0.146240 \rightarrow d = 0.146240$$

Hence,

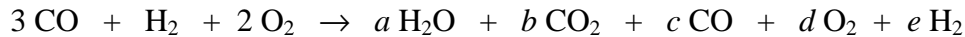
$$a = 1.0, \quad b = 2.70752, \quad c = 0.29248, \quad d = 0.14624, \quad n = 4.14624$$

The mole fractions are :

$$X_{\text{H}_2\text{O}} = 0.2412, \quad X_{\text{CO}_2} = 0.6530, \quad X_{\text{CO}} = 0.0705, \quad X_{\text{O}_2} = 0.0353$$

The final pressure is : $p_2 = 2.1667 n p_0 = 8.984$ bar

- (b) If the H_2O dissociation is very small, the mole fractions of the major species will hardly change. We therefore consider the chemical equation,



with a, b, c and d unchanged. Reaction 5 is : $-\text{H}_2 - \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} = 0$

The equilibrium constant is therefore given by,

$$K_{p5}(T_2) = \left(\frac{p_{\text{H}_2}}{p_0} \right)^{-1} \left(\frac{p_{\text{O}_2}}{p_0} \right)^{-1/2} \left(\frac{p_{\text{H}_2\text{O}}}{p_0} \right)^{+1}$$

where $p_0 = 1$ bar and $T_2 = 2600$ K. From the Data Book,

$$\ln(K_{p5}) = 4.647 \quad \rightarrow \quad K_{p5} = 104.27$$

Hence,

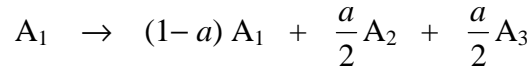
$$104.27 = \frac{(a/n)}{(e/n)(d/n)^{0.5} (p_2/p_0)^{0.5}}$$

As before, $p_2/p_0 = 2.1667 n$. Hence,

$$e \cong \frac{a}{104.7 \times (2.1667)^{0.5} \times d^{0.5}} = 0.01697 \quad \rightarrow \quad X_{\text{H}_2} \cong \frac{e}{n} = 0.0041$$

This is clearly very small and hence the approximate calculation is justified.

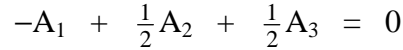
8(a) The dissociation of 1 mole of A_1 is represented by,



The total number of moles in the mixture = 1, and the partial pressures are given by,

$$p_1 = (1-a)p, \quad p_2 = \frac{a}{2}p, \quad p_3 = \frac{a}{2}p$$

The dissociation reaction is,



so the equilibrium constant is given by,

$$K(T) = \frac{(p_2/p_0)^{0.5} (p_3/p_0)^{0.5}}{(p_1/p_0)}$$

Substituting the expressions for the partial pressures,

$$K = \frac{(a/2)^{0.5} (a/2)^{0.5}}{(1-a)} \rightarrow a = \frac{2K}{2K+1}$$

Hence, the mole fractions are,

$$X_1 = \frac{1}{2K+1}, \quad X_2 = \frac{K}{2K+1}, \quad X_3 = \frac{K}{2K+1}$$

The molar enthalpy of the mixture is,

$$\bar{h} = \sum_{i=1}^3 X_i \bar{h}_i = \frac{\bar{h}_1 + K \bar{h}_2 + K \bar{h}_3}{(2K+1)}$$

(b) The isobaric molar heat capacity is,

$$\bar{c}_p = \left(\frac{\partial \bar{h}}{\partial T} \right)_p = \frac{1}{(2K+1)} \left[\left(\frac{\partial \bar{h}_1}{\partial T} \right)_p + K \left(\frac{\partial \bar{h}_2}{\partial T} \right)_p + K \left(\frac{\partial \bar{h}_3}{\partial T} \right)_p + (\bar{h}_2 + \bar{h}_3) \frac{dK}{dT} \right] - \frac{2(\bar{h}_1 + K \bar{h}_2 + K \bar{h}_3)}{(2K+1)^2} \frac{dK}{dT}$$

The isobaric molar heat capacities for the individual species are defined by,

$$\bar{c}_{p1} = \left(\frac{\partial \bar{h}_1}{\partial T} \right)_p \quad \bar{c}_{p2} = \left(\frac{\partial \bar{h}_2}{\partial T} \right)_p \quad \bar{c}_{p3} = \left(\frac{\partial \bar{h}_3}{\partial T} \right)_p$$

Hence,

$$\bar{c}_p = \frac{\bar{c}_{p1} + K\bar{c}_{p2} + K\bar{c}_{p3}}{(2K+1)} - \frac{(2\bar{h}_1 - \bar{h}_2 - \bar{h}_3)}{(2K+1)^2} \frac{dK}{dT}$$

We need to write this in terms of $\Delta\bar{H}_T$ which is the enthalpy change when 1 mole of A_1 dissociates completely at temperature T :

$$\Delta\bar{H}_T = -\bar{h}_1 + \frac{1}{2}\bar{h}_2 + \frac{1}{2}\bar{h}_3$$

Thus,

$$\bar{c}_p = \frac{\bar{c}_{p1} + K\bar{c}_{p2} + K\bar{c}_{p3}}{(2K+1)} + \frac{2\Delta\bar{H}_T}{(2K+1)^2} \frac{dK}{dT}$$

Introducing van't Hoff's equation,

$$\frac{d(\ln K)}{dT} = \frac{1}{K} \frac{dK}{dT} = \frac{\Delta\bar{H}_T}{\bar{R}T^2}$$

We obtain finally,

$$\bar{c}_p = \frac{\bar{c}_{p1} + K\bar{c}_{p2} + K\bar{c}_{p3}}{(2K+1)} + \frac{2K\bar{R}}{(2K+1)^2} \left(\frac{\Delta\bar{H}_T}{\bar{R}T} \right)^2$$

The first term can be written,

$$\frac{\bar{c}_{p1} + K\bar{c}_{p2} + K\bar{c}_{p3}}{(2K+1)} = \sum_{i=1}^3 X_i \bar{c}_{pi}$$

This is the molar specific heat capacity of the mixture in the absence of any chemical reaction. The second term represents the effect of the dissociation.

Because $K > 0$, the effect of the dissociation is always to increase \bar{c}_p and hence decrease the final temperature.