

Module 3A5: Thermodynamics

Notes on Examples Paper 2

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Abstract

This document outlines the methods used to answer each question on the second Thermodynamics examples paper. Some more general information is included for interest. This material is intended to complement to the more detailed worked solutions available in the official cribs. Statements of physical principles and definitions are highlighted in **bold**, while assumptions are *emphasised*.

Q1: Helmholtz function

(a)

Begin with the **definition** of specific Helmholtz function as stated, and put into differential form. Eliminate the entropy differential using the Tds **equation** and apply the boundary conditions to remove the temperature differential.

Aside. The Tds equation, or more formally the “fundamental thermodynamic relation”, incorporates both the **First** and **Second Laws** into one expression describing all changes of thermodynamic state for a system with a uniform temperature and pressure.

$$Tds = du - pdv \quad (1)$$

In Part I, you derive the Tds equation using the **Second Law** for a *reversible* process, that is $\delta S = \delta Q/T$. This is the easiest way to complete the derivation, but leads to some confusion as the equation is also true for irreversible processes. This must be so, because Eqn. (1) only includes thermodynamic state variables, which contain no information of the details of the process they are undergoing. This is not true of equations featuring, for example, Q .

(b)

First write the constant total volume and constant total mass **constraints** in differential form by differentiating the given expressions. Then differentiate the total Helmholtz function to get an expression for dF which is the quantity of interest. Combine these three equations and simplify. Don't forget the definitions of f , g and h . The question suggests that we need an expression in terms of the specific Gibbs function.

At equilibrium, the analysis in Lecture 5 shows that, for a system held at constant V and T , as in this question, the Helmholtz function is a minimum at equilibrium, that is $dF = 0$. If we imagine making an infinitesimal mass transfer between the phases, from the equilibrium position, dF should remain zero. Given this fact, inspection of your expression for dF will yield the equilibrium condition.

Q2: Clausius–Clapeyron equation

Begin by quoting the **Clausius–Clapeyron** equation from the lecture notes (you must remember this for the exam),

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

We want to find an expression for the ratio of saturated vapour pressures between two states, p_{s2}/p_{s1} . Since we have an expression for dp_s/dT we proceed by integrating with respect to T . It is stated that h_{fg} can be taken as a *constant*, but the dependency of v_{fg} on T is not known. The two approximations required to proceed are: water is *much denser* than steam (look in the tables if you are not convinced), and that the vapour phase behaves as a *perfect gas* (true in the limit of low pressure). Now we can perform the integration. We want to end up with terms in p_{si} , T_i , and constants.

Q3: Maxwell relation

(a)

The process for deriving a Maxwell relation is described in the lecture notes. Briefly,

1. Write an expression for a small change in the dependent thermodynamic variable (f in this case) in terms of partial derivatives with respect to the two independent thermodynamic variables (v and T in this case)
2. Write an expression for a small change in the dependent thermodynamic variable by differentiating its definition and manipulating using the Tds equation.
3. Compare the two to get a pair of first-derivative relations.
4. The Maxwell relation is found by differentiating again and applying equality of the mixed partial derivatives.

(b)

Give the *ideal gas* equation of state, we can directly evaluate the left-hand side of the Maxwell relation. We are interested in u , so must use the Tds **equation** to link the right-hand side of the Maxwell relation with u . Dividing through by v at constant T we arrive at an expression for $\partial u/\partial v|_T$, which can be integrated to get u , and then differentiated again (but with respect to T) to get c_v .

Q4: Characteristic equation of state

(a)

The p - v - T equation of state is just any expression relating these quantities for a particular substance. A more familiar p - v - T equation of state is $p v = RT$ for an ideal gas. Two thermodynamic variables are needed to define a state, and so any (physically correct) equation relating three thermodynamic variables completely characterises the thermodynamic properties of the substance.

We have $f = f(v, T)$, so it would be convenient if we could find an expression for pressure in terms of f and its derivatives with respect to v and T . One of the intermediate results from Q3 is helpful here.

(b)

Entropy can be found using another of the intermediate results from Q3. Then, internal energy can be found using the definition of f , and c_v by differentiation of u .

To reveal the significance of T_0 and v_0 , it is instructive to set $T = T_0$ and $v = v_0$ in the expressions derived above.

(c)

Starting from the right-hand side of the given equation,

$$c_p - c_v = \left. \frac{\partial h}{\partial T} \right|_p - c$$

using the definition of c_p and the value of $c_v = c$ from part (b). Now substituting $h = u + pv$ and splitting the differential,

$$\begin{aligned} c_p - c_v &= \left. \frac{\partial}{\partial T} [u + pv] \right|_p - c \\ c_p - c_v &= \left. \frac{\partial u}{\partial T} \right|_p + p \left. \frac{\partial v}{\partial T} \right|_p - c \end{aligned}$$

The end result retains the factor $\partial v/\partial T|_p$, which suggests that we can leave the second term on the right-hand side alone. Expanding the first $\partial u/\partial T|_p$ term using our

expression for u from part (b),

$$c_p - c_v = \frac{\partial}{\partial T} \left[c(T - T_0) - a \left(\frac{1}{v} - \frac{1}{v_0} \right) \right]_p - c$$

$$c_p - c_v = c - a \frac{\partial}{\partial T} \left[\frac{1}{v} \right]_p + p \frac{\partial v}{\partial T} \Big|_p - c$$

$$c_p - c_v = -a \frac{\partial}{\partial T} \left[\frac{1}{v} \right]_p + p \frac{\partial v}{\partial T} \Big|_p$$

If we are taking a partial differential with respect to T at constant p , because v is not then independent and will be a function of T the chain rule is required,

$$\frac{\partial}{\partial T} \left[\frac{1}{v} \right]_p = \frac{\partial v}{\partial T} \Big|_p \frac{\partial}{\partial v} \left[\frac{1}{v} \right]_p = \frac{-1}{v^2} \frac{\partial v}{\partial T} \Big|_p$$

so that the final expression is then,

$$c_p - c_v = \frac{a}{v^2} \frac{\partial v}{\partial T} \Big|_p + p \frac{\partial v}{\partial T} \Big|_p$$

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

$$c_p - c_v = \left(\frac{RT}{v - b} \right) \frac{\partial v}{\partial T} \Big|_p$$

using the expression for p in part (a).

Q5: van der Waals equation of state

This is, more or less, a mathematical exercise with little thermodynamics involved. b is the 'excluded volume' and, all other things being constant, leads to a larger specific volume of the non-ideal gas. This is the deviation from ideal gas behaviour (where molecules are modelled as point masses) due to the microscopic size of the molecule. a acts, all other things being equal, to reduce the pressure. The ideal gas model neglects intermolecular forces; the real attractive force of the molecules towards each other reduces the force exerted on the container.

Q6: Simple equilibrium

This is a basic equilibrium question, as in the lecture notes. In brief,

1. Write a general chemical equation for the reaction with n unknown coefficients for each of the n products.
2. Applying conservation of atoms will yield $n - 1$ equations; the system must be closed by introducing the equilibrium constant K_p , the value of which can be found in the Data Book.
3. Write an expression for K_p using partial pressures, then convert to mole fractions times the mixture pressure.

4. Solve the system of equations, by eliminating successive variables until one remains, then solve analytically or iteratively.

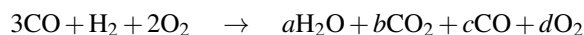
Because the stoichiometric coefficients sum to zero in this case, the mixture pressure does not appear in the expression for K_p . Physically, this is because the number of moles, and hence total volume, on each side of the reaction is the same.

Q7: Advanced equilibrium

(a)

We are instructed to *neglect dissociation* of H_2O , so we assume that the H_2 oxidation reaction goes to completion, or another way of stating this is that there is no H_2 present in the equilibrium mixture.

We are told that the CO and H_2 are in molar proportions 3:1, with *stoichiometric* O_2 . Looking at reaction number (7) in the Data Book, for each molecule of CO we need $\frac{1}{2}\text{O}_2$ for stoichiometric combustion. Looking at reaction number (5) in the Data Book, for each molecule of H_2 we also need $\frac{1}{2}\text{O}_2$ for stoichiometric combustion. So for 3 moles of CO and 1 of H_2 we need 2O_2 ,



From this equation, the 3 **atom balance** equations can be derived. It follows that $a = 1$ without further manipulation. The **expression for K_p** for reaction (7) is,

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

Remember that in this expression p_0 is not the mixture pressure. It is simply standard pressure, 1 bar, as stated next to the definition of K_p in the Data Book. Converting to mole fractions using the final mixture pressure p_2 , and $n = a + b + c + d$,

$$\begin{aligned} K_p &= \left(X_{\text{CO}} \frac{p_2}{p_0}\right)^{-1} \left(X_{\text{O}_2} \frac{p_2}{p_0}\right)^{-1/2} \left(X_{\text{CO}_2} \frac{p_2}{p_0}\right)^1 \\ K_p &= \left(\frac{c}{n} \frac{p_2}{p_0}\right)^{-1} \left(\frac{d}{n} \frac{p_2}{p_0}\right)^{-1/2} \left(\frac{b}{n} \frac{p_2}{p_0}\right)^1 \\ K_p &= \frac{b}{c} \sqrt{\frac{n p_0}{d p_2}} \end{aligned}$$

To proceed we need information on the final mixture pressure p_2 . We are told to assume that all species behave as *ideal gases*, suggesting that we should use the **ideal gas equation of state**. Initially,

$$p_1 V = n_1 \bar{R} T_1, \quad (2)$$

where p_1 and T_1 are the given initial pressure and temperature, R is the molar gas constant, and V is the volume of the *constant volume* combustor. The initial number of

moles can be set to $n_1 = 6$ based on the left-hand side of the chemical equation. After combustion,

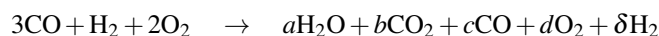
$$p_2V = n\bar{R}T_2, \quad (3)$$

where T_2 is the given final temperature at p_2 is the unknown final pressure. Taking the ratio of Eqns. (2) and (3) gives the final pressure as a function of n and other known quantities.

Now, the system of equations is close and can be solved iteratively.

(b)

Slight dissociation implies that the number of moles of the other products is barely changed, i.e. the percentage changes in a , b , c , d , and n are small. The chemical equation becomes,

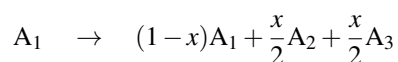


Writing the K_p **expression** for reaction (5), there is only one unknown δ .

Q8: van't Hoff's equation

(a)

There is not conservation of atom information in this question, but we know by *stoichiometry* that the number of moles of A_2 and A_3 must be equal. In this situation, the chemical equation is,



The **equilibrium constant** for this reaction is defined,

$$K(T) = \left(\frac{p_{A_1}}{p_0}\right)^{-1} \left(\frac{p_{A_2}}{p_0}\right)^{1/2} \left(\frac{p_{A_3}}{p_0}\right)^{1/2}$$

Substituting for the partial pressures

$$K(T) = \left(\frac{1-x}{1} \frac{p_2}{p_0}\right)^{-1} \left(\frac{x/2}{1} \frac{p_2}{p_0}\right)^{1/2} \left(\frac{x/2}{1} \frac{p_2}{p_0}\right)^{1/2},$$

$$K(T) = \frac{\sqrt{x/2}\sqrt{x/2}}{1-x},$$

which can be solved for x in terms of $K(T)$, and hence the mole fractions.

The molar enthalpy is simply a weighted sum of the mole fractions and molar enthalpies.

(b)

From the **definition of** \bar{c}_p ,

$$\bar{c}_p = \left. \frac{\partial \bar{h}}{\partial T} \right|_p = \frac{\partial}{\partial T} \left[\frac{\bar{h}_1 + K\bar{h}_2 + K\bar{h}_3}{2K+1} \right]_p.$$

After some manipulation using the product and chain rules,

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

The last term in brackets is just the enthalpy of reaction, $\Delta\bar{H}_T^0$. The dK/dT term can be eliminated using the **van't Hoff equation** to arrive at the given answer:

$$\bar{c}_p = \frac{\bar{c}_{p1} + K\bar{c}_{p2} + K\bar{c}_{p3}}{2K+1} + \frac{2K\bar{R}}{(2K+1)^2} \left(\frac{\Delta\bar{H}_T^0}{\bar{R}T} \right)^2.$$

The first term is a weighted sum of the molar specific heat capacities, i.e. the heat capacity at constant composition. The second term accounts for the shift in the composition as temperature changes. Because the second term is always positive, it increases the specific heat capacity. Then, for a given enthalpy change, the temperature change is reduced.