

Problem Set PS08

ISSUED: 3/16/99 Due: 3/23/00

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Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. We will run into a number of simple differential equation and it will be nice to be able to solve them in our heads. Many relations we will see during derivations will be what are called first order ordinary differential equations. (The rate laws of kinetics were of this type.) “First order” means that only a first derivative appears in the differential equation, “ordinary” means we are worried about only one independent variable. A common type first order differential equation is of the form

$$\frac{df}{dx} = P(x)Q(f),$$

where $P(x)$ is any function of x and $Q(f)$ is an explicit function of f . Equations of this type may be solved using a technique called separation of variables (n.b., this is not at all related to the separation of variables technique for solving partial differential equations like the Schrödinger for a particle in a 3D box). The procedure goes as follows. The dx is moved to the right hand side of the differential equation and $Q(f)$ to the left hand side,

$$\frac{df}{Q(f)} = P(x)dx,$$

then each side is integrated

$$\int \frac{df}{Q(f)} = \int P(x)dx.$$

This solves the differential equation (provide you can do the integrals). Note that the constant of integration associated with the f integration is combined with the constant of integration of the x integration. This constant can be determined if some other piece of information is know; that is, if we are given an initial condition or boundary condition. Use this technique to solve the following differential equations

- (a) $\frac{df}{dx} = c, f(x = 0) = 1$
- (b) $\frac{df}{dx} = -cx, f(x = 0) = 1$
- (c) $\frac{df}{dx} = \sin x, f(x = 0) = 1$
- (d) $\frac{df}{dx} = f, f(x = 0) = 1$
- (e) $\frac{df}{dx} = fx, f(x = 0) = 1$

Exercises

- Derive the virial series for a Berthelot gas by hand. Sketch a plot of the second virial coefficient. How does the second virial coefficient for the Berthelot gas compare to that of the van der Waals gas?
- Derive equations 17.19 and 17.20 of the notes.
- Use Eq. (17.46) to determine α/κ_T for a van der Waals gas.
- Derive an expression for the molar heat capacity at constant pressure for a van der Waals gas.
- A gas expands adiabatically from 1L to 2L. The temperature drops from 300.0K to 292.6K. What is the average constant volume molar heat capacity (\bar{C}_V)?
- A gas is described by the following equation of state: $PV_m = RT + \alpha P$. Show that the work done during reversible isothermal expansion is

$$w = RT \ln \left(\frac{V_2 - \alpha}{V_1 - \alpha} \right)$$

- It can be shown that for an ideal gas

$$\frac{\partial G}{\partial P} = V.$$

Replace V on the right hand side using the ideal gas law. Then solve the resulting differential equation to show that for an ideal gas the free energy is

$$G = RT \ln P + f(T),$$

where $f(T)$ is at most a function of T

- A simple model for particles in a centrifuge tube is to treat the particles of interest as an ideal “gas” (here empty space between particles is replaced by solution). The “centrifugal pressure,” P , is a function of the position (or height, h) of the particle in the test tube:

$$\frac{dP}{dh} = \frac{Mg}{V_m},$$

where M is the mass of the particle and g is the centrifugal force. The free energy of the particles is given by the results of the previous question but with the addition of a potential energy term based on the height in the test tube,

$$G = RT \ln P + f(T) + Mgh,$$

If the centrifugal pressure at the bottom of the tube (at $h = 0$) is P_0 and the tube is at a constant temperature show that the centrifugal pressure at any height h is

$$P = P_0 e^{-\frac{Mgh}{RT}}.$$

Solve the problem two different ways. First, solve the differential equation for P . Second use the free energy functions.

Conceptual Problems

10. Explain how the Joule expansion experiment differs from the Joule–Tomson experiment (See legacy projects by Cara Hagen and Stephanie Collins (fall99)).

Computer Problems

11. Use MATHEMATICA to derive the virial series for the van der Waals, Berthelot, Dieterici and Redlich–Kwang gases.

① ② $\frac{df}{dx} = c \Rightarrow \int df = c dx \Rightarrow f = cx + a$

$f(0) = 1 = c \cdot 0 + a \Rightarrow a = 1 \Rightarrow f = cx + 1$

③ $\frac{df}{dx} = -cx \Rightarrow \int df = -cx dx \Rightarrow f = -\frac{cx^2}{2} + a$

$f(0) = 1 = -\frac{c}{2} \cdot 0^2 + a \Rightarrow a = 1 \Rightarrow f = -\frac{cx^2}{2} + 1$

④ $\frac{df}{dx} = \sin x \Rightarrow \int df = \sin x dx \Rightarrow f = -\cos x + a$

$f(0) = 1 = -\cos 0 + a \Rightarrow a = 2 \Rightarrow f = -\cos x + 2$

⑤ $\frac{df}{dx} = f \Rightarrow \int \frac{df}{f} = dx \Rightarrow \ln f = x + a$

$f = e^{x+a} = e^x e^a = A e^x$

$f(0) = 1 = A e^0 \Rightarrow A = 1 \Rightarrow f = e^x$

⑥ $\frac{df}{dx} = fx \Rightarrow \int \frac{df}{f} = x dx \Rightarrow \ln f = \frac{x^2}{2} + a$

$f = e^{\frac{x^2}{2} + a} = A e^{\frac{x^2}{2}} \Rightarrow f(0) = 1 = A e^0 \Rightarrow A = 1 \Rightarrow f = e^{\frac{x^2}{2}}$

③ The two ways of writing the virial series are

(i) $Z = 1 + B\left(\frac{1}{V_m}\right) + C\left(\frac{1}{V_m}\right)^2 + \dots$

(ii) $Z = 1 + B'P + C'P^2 + \dots$

Using (i) we have

$P = \frac{RT}{V_m} + \frac{RTB}{V_m^2} + \frac{RTC}{V_m^3} + \dots$

Subbing this into (ii)

$Z = 1 + B'\left(\frac{RT}{V_m} + \frac{RTB}{V_m^2} + \dots\right) + C'\left(\frac{RT}{V_m} + \frac{RTB}{V_m^2} + \dots\right)^2 + \dots$

$Z = 1 + B'RT \frac{1}{V_m} + (RTBB' + C'(RT)^2) \frac{1}{V_m^2} + O\left(\frac{1}{V_m^3}\right)$

Comparing (i) and (ii) term by term we get

$B = B'RT \quad C = RTBB' + C'(RT)^2$

$B' = \frac{B}{RT}$

$C' = \frac{C}{(RT)^2} - \frac{BB'}{RT} \quad B' = \frac{B}{RT}$

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

2. Berthelot gas

$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$

$\frac{V_m P}{RT} = Z = \frac{V_m RT}{RT(V_m - b)} - \frac{V_m a}{RT^2 V_m^2}$

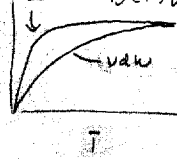
$Z = \frac{1}{\left(1 - \frac{b}{V_m}\right)} - \frac{a}{RT^2 V_m}$

$Z = \left(1 + \left(\frac{b}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \dots\right) - \frac{a}{RT^2 V_m}$

$Z = 1 + \left(b - \frac{a}{RT}\right)\left(\frac{1}{V_m}\right) + b^2\left(\frac{1}{V_m}\right)^2 + b^3\left(\frac{1}{V_m}\right)^3 + \dots$

$B(T)_{Berth} = b - \frac{a}{RT^2}$

$B(T)_{vdw} = b - \frac{a}{RT}$



④ $\frac{d}{dT} \left(\frac{\partial P}{\partial T} \right)_V$

$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$

$\frac{d}{dT} \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - b}$

⑤ $C_{P,m} = C_{V,m} + T \left(\frac{\partial C_{V,m}}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{V,m}$
 vdw eq is explicit in P so

$C_{P,m} = C_{V,m} - T \left(\frac{\partial P}{\partial T} \right)_{V,m}^2 \left(\frac{\partial V}{\partial P} \right)_T$

$\left(\frac{\partial P}{\partial T} \right)_{V,m} = \frac{C_{V,m} - T \left(\frac{R^2}{(V_m - b)^2} \right)}{-\frac{RT}{(V_m - b)^2} + \frac{a}{V_m^3}}$

⑥ from (17, 71)

$$\bar{C}_{vm} \ln \frac{292.6}{300.2} = -R \ln \frac{P}{P_0}$$

$$-2.49 \times 10^{-2} C_{vm} = -8.314 (0.695)$$

$$C_{vm} = 233 \frac{J}{\text{mol} \cdot K} \leftarrow \text{not realistic number}$$

⑦

$$w = - \int_{v_1}^{v_2} P dv \quad P = \frac{RT}{v_m - a}$$

$$w = - \int_{v_1}^{v_2} \frac{RT}{v - a} dv = -RT \ln \frac{v_2 - a}{v_1 - a} \quad \checkmark$$

⑧

$$\frac{dG}{dP} = V = \frac{nRT}{P} \quad \int dG = \frac{nRT}{P} dP$$

$$G = nRT \ln P + f(T)$$

The constant of integration is a function of temperature.

⑨

$$\frac{dP}{dh} = -\frac{Mg}{v_m} = -\frac{Mg}{\frac{RT}{P}} \Rightarrow \int \frac{dP}{P} = -\frac{Mg}{RT} dh$$

$$\ln P = -\frac{Mgh}{RT} + c \quad P = e^{-\frac{Mgh}{RT} + c} = \frac{e^c}{P_0} e^{-\frac{Mgh}{RT}} = P_0 e^{-\frac{Mgh}{RT}}$$

$$\text{at any } h \quad G = RT \ln P + f(T) + mgh$$

$$\text{at } h=0 \quad G = RT \ln P_0 + f(T)$$

$$RT \ln P_0 = RT \ln P + mgh$$

$$\ln P - \ln P_0 = -\frac{mgh}{RT}$$

$$\ln \frac{P}{P_0} = -\frac{mgh}{RT}$$

$$P = P_0 e^{-\frac{mgh}{RT}} \quad \checkmark$$

10 your words

11 your mathematics

$$\left(\frac{P_1}{P_2} \right)^{\frac{R}{C_p - C_v}} = \left(\frac{T_1}{T_2} \right)^{\frac{R}{C_p - C_v}}$$

$$\ln \left(\frac{P_1}{P_2} \right)^{\frac{R}{C_p - C_v}} = \ln \left(\frac{T_1}{T_2} \right)^{\frac{R}{C_p - C_v}}$$

$$\frac{R}{C_p - C_v} \ln \left(\frac{P_1}{P_2} \right) = \frac{R}{C_p - C_v} \ln \left(\frac{T_1}{T_2} \right)$$

$$\ln \left(\frac{P_1}{P_2} \right) = \ln \left(\frac{T_1}{T_2} \right)$$

$$\left(\frac{P_1}{P_2} \right)^{\frac{R}{C_p - C_v}} = \left(\frac{T_1}{T_2} \right)^{\frac{R}{C_p - C_v}}$$