

**CYL100 2013–14 I semester Homework 1 Solutions**

August 9, 2013

1. Dieterici's equation of state for a gas is  $P(V - b) \exp(a/RVT) = RT$ , where  $a$ ,  $b$ , and  $R$  are constants. Determine  $(\partial V/\partial T)$ ,  $(\partial T/\partial P)$ , and  $(\partial P/\partial V)$  and verify that  $(\partial V/\partial T) (\partial T/\partial P) (\partial P/\partial V) = -1$ .

First, I will show you a nifty trick to evaluate some of these “ugly” partial derivatives of implicit functions,  $f(x, y, z) = 0$  - it is possible that some of you know it. Suppose that  $f(x, y, z)$  is differentiable and that the equation  $f(x, y, z) = 0$  determines  $z$  as a differentiable function of  $x$  and  $y$ , then, at points where  $f_z \neq 0$ ,

$$\left(\frac{\partial z}{\partial x}\right)_y = -\frac{f_x}{f_z}$$

and

$$\left(\frac{\partial z}{\partial y}\right)_x = -\frac{f_y}{f_z}.$$

Here  $f_z$  is the “simple” derivative of  $f(x, y, z)$  wrt  $z$  keeping  $x$  and  $y$  constant. Other partial derivatives can be written similarly. For example,

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{f_x}{f_y}.$$

How does one show this result? If  $f(x, y, z) = 0$ , then it means that  $f(x, y, g(x, y)) = 0$  for all  $(x, y)$  in the domain of  $f$ . If  $f$  and  $g$  are differentiable, then we can use the chain rule to differentiate  $f(x, y, z) = 0$  as follows:

$$\frac{\partial f}{\partial x} \frac{\partial x}{\partial x} + \frac{\partial f}{\partial y} \frac{\partial y}{\partial x} + \frac{\partial f}{\partial z} \frac{\partial z}{\partial x} = 0$$

But

$$\frac{\partial x}{\partial x} = 1 \quad \text{and} \quad \frac{\partial y}{\partial x} = 0,$$

which yields

$$\frac{\partial f}{\partial x} + \frac{\partial f}{\partial z} \frac{\partial z}{\partial x} = 0,$$

or

$$\frac{\partial z}{\partial x} = -\frac{f_x}{f_z}.$$

Armed with this trick, the problem at hand is reduced to determining  $f_P$ ,  $f_V$ , and  $f_T$ , which turn out to be:

$$\begin{aligned} f_T &= -P(V - b) \exp(a/RVT) \frac{RV^2}{a} - R \\ f_V &= P \exp(a/RVT) - P(V - b) \exp(a/RVT) RV^2 T/a \\ f_P &= (V - b) \exp(a/RVT) \end{aligned}$$

The required partial derivatives are determined by taking the appropriate ratios. For example,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{f_T}{f_P}.$$

The others can be obtained similarly with minimum effort.

Proving the cyclic rule is straightforward too - it is just a matter of multiplication.

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = \left(-\frac{f_T}{f_P}\right) \times \left(-\frac{f_V}{f_T}\right) \times \left(-\frac{f_P}{f_V}\right) = -1$$

For fun you could try to extend this rule for functions of the type  $f(w, x, y, z) = 0$ .

2. Given the equation of state  $V = V_0(1 + \alpha T - \beta P)$  for a liquid where  $V_0$ ,  $\alpha$ , and  $\beta$  are constants: (a) Derive an expression for the work done when the pressure on the liquid is increased reversibly and isothermally from  $P_1$  to  $P_2$ . (b) Use your equation to evaluate the work done when 2.00 mol of water ( $\beta = 4.67 \times 10^{-5} \text{ atm}^{-1}$ ) is subjected to an increase in pressure from 1.00 atm to 2.00 atm at 25 °C.

(a)

$$\begin{aligned} V &= V_0(1 + \alpha T - \beta P) \\ dV &= -\beta V_0 dP \end{aligned}$$

$$w = - \int P dV = \beta \int P dP = \frac{\beta V_0}{2} (P_2^2 - P_1^2)$$

(b)

$$w = \frac{(0.0360L)(4.67 \times 10^{-5} \text{atm}^{-1})}{2} [2.00^2 - 1.00^2] \text{atm}^2$$

$$w = 2.52 \times 10^{-6} \text{L atm}$$

3. When you open a can of your favorite aerated drink, compressed  $\text{CO}_2$  expands irreversibly against the atmosphere as it bubbles up through the drink. Assume that the process is adiabatic and that the  $\text{CO}_2$  has an initial pressure of 3 bar. Take  $\text{CO}_2$  to be an ideal gas, with a constant heat capacity of  $C_P = 37 \text{ J}/(\text{mol K})$ . What is the final temperature of the  $\text{CO}_2$  after it has reached atmospheric pressure?

We assume that the initial temperature is  $5^\circ\text{C}$ , which is a reasonable temperature for an aerated drink.

$$\Delta U = w$$

$$C_v(T_2 - T_1) = - \int P_{ext} dV = -P_{ext}(V_2 - V_1)$$

Assuming that  $\text{CO}_2$  is an ideal gas,

$$C_v(T_2 - T_1) = -P_{ext} \left[ \frac{T_2}{P_2} - \frac{T_1}{P_1} \right] = -R \left[ T_2 - \frac{P_2 T_1}{P_1} \right],$$

where the equation was simplified because the final pressure  $P_2$  is equal to the constant external pressure  $P_{ext}$ . Simplifying

$$T_2 \left( 1 + \frac{R}{C_v} \right) = T_1 \left( 1 + \frac{R P_2}{C_v P_1} \right)$$

$$T_2 = T_1 \left( 1 + \frac{R P_2}{C_v P_1} \right) \frac{C_v}{C_P} = 237 \text{K}$$

4. Consider a piston-cylinder assembly that contains 1 mole of ideal gas A. The system is well insulated. Its initial volume is 10 L and initial pressure, 2 bar. The gas is allowed to expand against a constant external pressure of 1 bar until it reaches mechanical equilibrium. Is this a reversible process? What is the final temperature of the system? How much work was obtained? For gas A  $C_V = 5/2R$ .

$$\Delta = w$$

Let  $n_1 = n_2 = n$ . The energy balance can be rewritten as

$$n \int_{T_1}^{T_2} C_v dT = - \int_{V_1}^{V_2} P_{ext} dV$$

From the ideal gas law we get  $V_2$  and  $T_1$ , and using  $P_{ext} = P_2$ , and simplifying gives

$$T_2 = \frac{(P_2 + \frac{5}{2}P_1) V_1}{\frac{7}{2}nR} = 206 \text{K}$$

To find the value of the work, the energy balance can be used

$$w = nC_v(T_2 - T_1)$$

with  $T_1 = \frac{P_1 V_1}{nR} = 241 \text{K}$ , which gives  $w = -727 \text{ J}$ .

5. For the well-insulated piston-cylinder assembly containing 1 mole of ideal gas described in the previous problem, describe the process by which you can obtain the maximum work from the system. Calculate the value for the work. What is the final temperature? Explain the difference, if any, in the final temperature of the gas in this problem and the previous one.

The maximum work is obtained through a reversible expansion of the gas in the piston. The system is well-insulated so the heat transfer is zero. The energy balance reduces to  $\Delta U = w$ . For this adiabatic reversible expansion

$$w = \frac{1}{\gamma - 1} [P_2 V_2 - P_1 V_1].$$

To calculate  $w$ ,  $V_2$  must be found. For an adiabatic reversible process, the relation  $PV^\gamma = \text{constant}$  holds. Therefore,

$$V_2 = \left( \frac{P_1}{P_2} V_1^\gamma \right)^{1/\gamma} = 16.4L$$

This yields

$$w = -9L \text{ bar} = -900J$$

6. At high densities the molecules themselves make up an appreciable fraction of the available volume, and an equation of state of 1 mol of gas can be written in the form  $P(V - b) = RT$ , where 'b' is a constant which is related to the size of the molecules. (i) Calculate the work done when 1 mole of this nonideal gas at 298 K is compressed reversibly and isothermally from 22.4 L to 0.224 L if 'b' is 0.04L. (ii) What is the work done if the gas behaves ideally in (i) and explain why the answers differ in (i) and (ii).

(i)

$$w = - \int_{V_1}^{V_2} P dV = -RT \ln \frac{V_2 - b}{V_1 - b}$$

(ii)

$$w = RT \ln \frac{V_2}{V_1}$$

The difference arises due to the volume correction.

7. For each of the following processes deduce whether each of the quantities  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  is positive, zero, or negative. (a) Reversible melting of solid benzene at 1 atm and the normal melting point. (b) Reversible melting of ice at 1 atm and 0°C. (c) Reversible adiabatic expansion of a perfect gas. (d) Reversible isothermal expansion of a perfect gas. (e) Adiabatic expansion of a perfect gas into a vacuum. (f) Reversible heating of a perfect gas at constant  $P$ . (g) Reversible cooling of a perfect gas at constant  $V$ .

$q$	$w$	$\Delta H$	$\Delta U$
+	-	+	+
+	+	+	+
0	-	-	-
+	-	0	0
0	0	0	0
+	-	+	+
-	0	-	-

This problem requires a little bit more thought than you might first imagine. The things to note that  $\Delta U$  and  $\Delta H$  are not always zero for isothermal processes. The expansion work when condensed phases are involved is close to but not equal to zero - the sign is dependent on the densities of the phases involved.

8. The isothermal compressibility of lead is  $2.3 \times 10^{-6} \text{ atm}^{-1}$ . A cube of lead of 10 cm length at 298K is inserted under 1000m of water where the temperature is 268K. Calculate the change in the volume of the cube given that the mean density of water is  $1.03 \text{ g cm}^{-3}$  and  $\alpha_{Pb}$  is  $8.61 \times 10^{-5}$ .

For  $V(T, P)$

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

In terms of  $\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$  and  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$

$$dV = \alpha V dT - \beta V dP$$

$$\int_{V_1}^{V_2} \frac{dV}{V} = \alpha \int_{T_1}^{T_2} dT - \beta \int_{P_1}^{P_2} dP$$

where  $P_2 - P_1 = 1000\text{m} \times 10\text{m s}^{-2} \times 1030\text{kg m}^{-3} = 1.03 \times 10^7 \text{ Pa}$  is the pressure exerted by 1 km of water in addition to the atmospheric pressure.

$$\ln \frac{V_2}{V_1} = \alpha(T_2 - T_1) - \beta(P_2 - P_1)$$

9. The molar heat capacity of oxygen at constant pressure for temperatures in the range 300 to 400 K and for low or moderate pressures can be approximated as  $C_P(\text{J mol}^{-1} \text{K}^{-1}) = 25.73 + 0.013T$ . (a) Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  when 2 mol of  $\text{O}_2$  is reversibly heated from 27 to 127 °C with  $P$  held fixed at 1 atm. (b) Repeat the calculation if the same change is effected at constant  $V$ .

For lack of information we will take it that oxygen behaves ideally.

(a)

$$q = \Delta H = \int_{T_1}^{T_2} C_P dT = 25.73(T_2 - T_1) + 0.013/2(T_2^2 - T_1^2)$$

$$w = -P_{ext}(V_2 - V_1) = -nR(T_2 - T_1)$$

$$\Delta U = q + w$$

(b)  $\Delta H$  and  $\Delta U$  are identical to (a),  $w = 0$ , and  $q = \Delta U$ .

10. Read the following statements *carefully* and decide whether (and why) they are true or false giving your thermodynamic reasoning. If the statement is false, you may either state which law or laws of thermodynamics it violates or provide a physical counter example or any other plausible physical reason. Finally, correct the false statement with a clarifying phrase that makes the statement true.

(i) The internal energy of a system and its surroundings is not conserved during an irreversible process, but it is conserved for reversible processes.

False. Energy is conserved no matter what process, reversible or irreversible, occurs.

(ii) No heat transfer occurs when liquid water is reversibly and isothermally compressed.

False. Although small, this is non-zero because  $\delta q = dU - \delta w$  and  $dU$  and  $\delta w$  are not necessarily equal.

(iii) If in a reversible process the temperature of one mole of an ideal gas increases by 1°C, the work done on the gas must be numerically equal to the molar heat capacity at constant volume,  $C_V$ .

False. Only if it is adiabatic.

(iv) If an ideal gas increases its volume by 1 cubic meter at a constant pressure of 1 Newton per square meter, then its internal energy decreases by 1 Joule.

False. Again, only if it is adiabatic.

(v) Melting of any material is an endothermic process.

True. Breaking of bonds, which accompanies melting, requires energy.