

## 8.6: Problems

### ? Problem 8.6.1

Given a generic equation of state  $P = P(V, T, n)$ , explain how you can obtain the derivative

$$\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

using the properties of partial derivatives we learned in this chapter.

### ? Problem 8.6.2

The thermodynamic equation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

shows how the internal energy of a system varies with the volume at constant temperature.

Prove that

1.  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  for an ideal gas.
2.  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$  for one mole of van der Waals gas (Equation 8.6.2)

### ? Problem 8.6.3

Consider one mole of a van der Waals gas (Equation 8.6.2) and show that

$$\left(\frac{\partial^2 P}{\partial V \partial T}\right) = \left(\frac{\partial^2 P}{\partial T \partial V}\right)$$

### ? Problem 8.6.4

Consider a van der Waals gas (Equation 8.6.2) and show that

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{\left(P - \frac{n^2 a}{V^2} + \frac{2n^3 ab}{V^3}\right)}$$

Hint: Calculate derivatives that are easier to obtain and use the properties of partial derivatives to get the one the problem asks for. Do not use the answer in your derivation; obtain the derivative assuming you don't know the answer and simplify your expression until it looks like the equation above.

### ? Problem 8.6.5

From the definitions of expansion coefficient ( $\alpha$ ) and isothermal compressibility ( $\kappa$ ):

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,n}$$

and

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,n}$$

prove that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{\alpha}{\kappa}$$

independently of the equation of state used.

Note: A common mistake in this problem is to assume a particular equation of state. Use the cycle rule to find the required relationship independently of any particular equation of state.

### ? Problem 8.6.6

Derive an equation similar to Equation 8.6.1, but that relates

$$\left(\frac{\partial f}{\partial y}\right)_x$$

with

$$\left(\frac{\partial f}{\partial r}\right)_\theta$$

and

$$\left(\frac{\partial f}{\partial \theta}\right)_r$$

### ? Problem 8.6.7

(Extra-credit level)

The expression:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

is known as the Laplacian operator in two dimensions.

When applied to a function  $f(x, y)$ , we get:

$$\nabla^2 f(x, y) = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2}$$

Express  $\nabla^2$  in polar coordinates (2D) assuming the special case where  $r = a$  is a constant.

### ? Problem 8.6.8

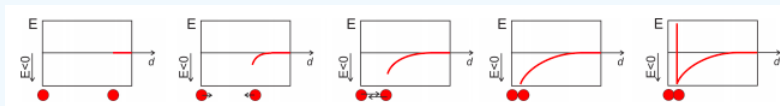
Calculate  $\int_0^1 \int_1^2 \int_0^2 (x^2 + yz) \, dx \, dy \, dz$ . Try three different orders of integration and verify you always get the same result.

### ? Problem 8.6.9

Calculate  $\int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-r} r^5 \sin \theta \, dr \, d\theta \, d\phi$ . Use only the formula sheet.

### ? Problem 8.6.10

How would Figure 8.5.2, reproduced below, look like for an ideal gas? Sketch the potential energy as a function of the distance between the atoms.



### ? Problem 8.6.11

From everything we learned in this chapter, and without doing any math, we should be able to calculate the sign ( $>0$ ,  $<0$ , or  $0$ ) of the following derivatives:

For an ideal gas:

$$\left(\frac{\partial U}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n}$$

For a van der Waals gas:

$$\left(\frac{\partial U}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n}$$

Be sure you can write a short sentence explaining your answers.

### ? Problem 8.6.12

The critical point is the state at which the liquid and gas phases of a substance first become indistinguishable. A gas above the critical temperature will never condense into a liquid, no matter how much pressure is applied. Mathematically, at the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = 0$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,n} = 0$$

Obtain the critical constants of a van der Waals gas (Equation 8.6.2) in terms of the parameters  $a$  and  $b$ .

Hint: obtain the first and second derivatives of  $P$  with respect to  $V$ , make them equal to zero, and obtain  $T_c$  and  $V_c$  from these equations. Finally, replace these expressions in Equation 8.6.2 to obtain  $P_c$ .

### 📌 Note

As derived in Section 8.3,

$$\left(\frac{\partial f}{\partial x}\right)_y = \cos\theta \left(\frac{\partial f}{\partial r}\right)_\theta - \frac{\sin\theta}{r} \left(\frac{\partial f}{\partial \theta}\right)_r \quad (8.6.1)$$

As defined in Section 8.5, the Van der Waals is defined as:

$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 \quad (8.6.2)$$

1. If you are not familiar with this you need to read about it before moving on

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