

1.12: The Equation of State

Note

From the last section, the cycle rule is defined as follows:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \quad (1.12.1)$$

The thermodynamic state of a system, such as a fluid, is defined by specifying a set of measurable properties sufficient so that all remaining properties are determined. For example, if you have a container full of a gas, you may specify the pressure, temperature and number of moles, and this should be sufficient for you to calculate other properties such as the density and the volume. In other words, the temperature (T), number of moles (n), volume (V) and pressure (P) are not all independent variables.

Ideal Gas Equation of State

To make sense of this statement, let's consider an ideal gas. You know from your introductory chemistry courses¹ that temperature, number of moles, volume and pressure are related through a universal constant R :

$$P = \frac{nRT}{V} \quad (1.12.2)$$

If P is expressed in atmospheres, V in liters, and T in Kelvin, then $R = 0.082 \frac{\text{L} \times \text{atm}}{\text{K} \times \text{mol}}$

This expression tells you that the four variables cannot be changed independently. If you know three of them, you also know the fourth.

Equation 1.12.2 is one particular case of what is known as an **equation of state**. An equation of state is an expression relating the density of a fluid with its temperature and pressure. Note that the density is related to the number of moles and the volume, so it takes care of these two variables together. There is no single equation of state that predicts the behavior of all substances under all conditions. Equation 1.12.2, for example, is a good approximation for non polar gases at low densities (low pressures and high temperatures). Other more sophisticated equations are better suited to describe other systems in other conditions, but there is no universal equation of state.

In general, for a simple fluid, an equation of state will be a relationship between P and the variables T , V and n :

$$P = P(T, V, n) = P(T, V_m),$$

where V_m is the molar volume, V/n . The molar volume is sometimes written as \bar{V} . For example, Equation 1.12.2 can be rewritten as

$$P = \frac{RT}{\bar{V}}.$$

Let's 'play' with the equation of state for an ideal gas. The partial derivative $\left(\frac{\partial P}{\partial T}\right)_{V,n}$ represents how the pressure changes as we change the temperature of the container at constant volume and constant n :

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

It is a relief that the derivative is positive, because we know that an increase in temperature causes an increase in pressure! This also tells us that if we increase the temperature by a small amount, the increase in pressure will be larger in a small container than in a large container.

The partial derivative $\left(\frac{\partial P}{\partial V}\right)_{T,n}$ represents how the pressure changes as we change the volume of the container at constant temperature and constant n :

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

Again, we are happy to see the derivative is negative. If we increase the volume we should see a decrease in pressure as long as the temperature is held constant. This is not too different from squeezing a balloon (don't try this at home!).

We can also write an equation that represents how the volume changes with a change in pressure: $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. From Equation 1.12.2,

$$V = \frac{nRT}{P}$$

and therefore:

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

Let's compare these two derivatives:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = -\frac{nRT}{P^2} = -\frac{nRT}{(nRT/V)^2} = -\frac{V^2}{nRT} = \frac{1}{\left(\frac{\partial P}{\partial V}\right)_{T,n}}$$

Surprised? You shouldn't be based on the inverse rule! (Equation ???). Note that this works because we hold the same variables constant in both cases.

Now, you may argue that the inverse rule is not particularly useful because it doesn't take a lot of work to solve for V and perform $\left(\frac{\partial V}{\partial P}\right)_{T,n}$.

Dieterici's Equation of State

Let's consider a more complex equation of state known as Dieterici's equation of state for a real gas:

$$P = \frac{RT}{\bar{V} - b} e^{-a/(R\bar{V}T)}$$

Here, a and b are constants that depend on the particular gas (e.g. whether we are considering H_2 or CO_2). Let's say you are asked to obtain $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. What do you do? Do you find the inverse rule useful now?

Let's go back to the ideal gas, and calculate other partial derivatives:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = -\frac{nRT}{V^2} \quad (1.12.3)$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{P} \quad (1.12.4)$$

$$\left(\frac{\partial T}{\partial P}\right)_{V,n} = \frac{V}{nR} \quad (1.12.5)$$

Let's calculate the product:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} \left(\frac{\partial V}{\partial T}\right)_{P,n} \left(\frac{\partial T}{\partial P}\right)_{V,n} = -\frac{nRT}{V^2} \frac{nR}{P} \frac{V}{nR} = -\frac{nRT}{VP} = -1$$

In the last step, we used Equation 1.12.2 Surprised? You shouldn't be based on the cycle rule! (Equation 1.12.1). Again, this is not particularly useful for an ideal gas, but let's think about Dieterici's equation again and let's assume that you are interested in

calculating $\left(\frac{\partial V}{\partial T}\right)_{P,n}$. What would you do?

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