
Appendix: A Chemistry Primer

A pure substance is one with a definite chemical formula, *e.g.*, N_2 or H_2O . Atomic constituents, like N or H or O each have an “atomic weight”, a number that can be found in the periodic table of elements. Hydrogen, H, has an atomic weight of 1 and oxygen, O, an atomic weight of 16. The “molecular weight” of the combine, H_2O is just the sum of weights of 2 hydrogen atoms and 1 oxygen atom, thus, 18.

The unit for atomic weight is the *atomic mass unit*, an exceedingly small quantity. One needs a lot of molecules to have enough to measure. In fact, it takes 6×10^{23} atomic mass units to amount to just 1 gram of material¹. It follows that 6×10^{23} molecules of any pure substance will yield an amount of material, in grams, that is the same as its molecular weight. This quantity of pure material is called a mole of the substance.² Hence, a mole of water contains 18 grams of water, about 18 milliliters of water at room temperature.

When a quantity of a pure substance in a container is in fluid form, either liquid or gas, its **state** is determined by its temperature, T , its pressure, p , and its volume, V . Temperature is measured in degrees Kelvin, $^\circ\text{K}$, pressure in atmospheres, and volume in liters.

Together with the number of moles, n , these measurable state quantities are connected by an **equation of state**:

$$p = p(T, V, n). \quad (1)$$

The variables in (1), pressure, temperature, volume and mole-count, are all positive numbers.

Each substance in fluid form has its own peculiar equation of state. The simplest equation of state is the **ideal gas law**:

$$p = \frac{nRT}{V}. \quad (2)$$

where R is the **gas constant**.³ This equation of state is often quoted as holding for many gases around 273°K (0°F) and 1 atmosphere. But equations of state for liquids in wide temperature ranges are hard to come by.

Chemists insist that *every* equation of state be “positively-homogeneous of degree 0 in n and V ”. This mouthful means that for every positive number λ , and fixed temperature, T_0 , the formula in (1) satisfies

$$p(T_0, \lambda V, \lambda n) = p(T_0, V, n).$$

For example, for fixed temperature, twice as many molecules in twice the volume produce the same pressure.⁴

For n moles of a pure substance, chemists exploit this requirement by taking $\lambda = 1/n$. Then

$$p(T, V/n, 1) = p(T, V, n).$$

¹The multiplier 6×10^{23} is called Avogadro’s number.

²For emphasis, a “gram-mole”.

³ $R = 0.08206$ liter-atmospheres per degree Kelvin per mole

⁴In chemical language, p is an “intensive” function of n and V .

Setting $v = V/n$, they suppress the 1 and write

$$p(T, V/n, 1) = p(T, v),$$

so that

$$p(T, V, n) = p(T, v).$$

The new variable, v , the **molar volume** of the substance, is measured in liters per mole. The simpler looking equation

$$p = p(T, v) \tag{3}$$

is called the **molar equation of state** for the pure substance. In the case of the ideal gas law, the molar equation of state is

$$p = \frac{RT}{v}.$$

No matter which molar equation of state might be employed, it is *always* assumed that for fixed temperature, pressure is a decreasing function of molar volume, provided the molar volume changes are small. That is,

Increasing Volume \Leftrightarrow Decreasing Pressure (IV=DP)

If v_2 is slightly larger than v_1 , then $p(T_0, v_2)$ is slightly smaller than $p(T_0, v_1)$.

The failure of the ideal gas law to account for the behaviour of many gases, to say nothing of liquids, prompted the invention of other models. By taking account of certain microscopic properties of fluids (gas or liquid), the Dutch physicist, Johannes van der Waals formulated an important variation on the ideal gas law. For any particular species, the van der Waals molar equation of state is

van der Waals

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

In this formula, each species of fluid has its own particular values for the constants, a and b . For carbon dioxide, CO_2 , $a = 3.592 \text{ liter}^2\text{-atmospheres}$ and $b = 0.04267 \text{ liters}$.⁵

Another important characteristic function for a fluid is its **heat capacity**. In fact, there are two standard versions of heat capacity, depending on how the heating process is managed. In the first of these, a single mole of gas is confined in a strong vessel so that even if we heat the gas, its volume does not change. In this situation, the amount of heat required to raise

⁵Each of these two parameters has a physical interpretation that we will examine later.

the temperature of the gas by 1°K is called the heat capacity at constant volume of the gas.

⁶ This particular (molar) heat capacity is denoted c_v .

In chemical reactions, a mix of various pure substances combines to yield a mix of other pure substances. The simplest of these reactions is a phase change. ⁷ During a phase change, small portions of a pure substance in one molar state, (T, v_1) , continually reappear in another state, (T, v_2) at the same temperature *and* pressure.

“Boiling” is the commonly observed phase change of water at $T_0 = 373.2^\circ\text{K}$ and $p_0 = 1$ atmosphere. At this temperature and pressure, the molar volume of liquid water is 0.0188 liters and the molar volume of steam is 30.1 liters.⁸

The phase change of water just mentioned is an “equilibrium phase change”. Once both liquid water and steam are present at an equilibrium pressure and temperature, these two state variables for the two phases will move in lock-step against any application of heat or mechanical effort. ⁹

An equilibrium phase change of *any* fluid, forces a linkage¹⁰ of pressure and temperature to one another by a **vapor pressure** function:¹¹

$$p = p_{\text{vp}}(T). \quad (\text{VP})$$

The vapor pressure of water at 373.2°K is 1 atmosphere.

As illustrated by boiling water, the most commonly encountered conditions for such equilibrium phase changes are constant temperature and, therefore, constant pressure. That is, $T = T_0 = \text{constant}$, so that

$$p(T_0, v_1) = p(T_0, v_2) = p_{\text{vp}}(T_0) = \text{constant}.$$

Formula (VP) is *not* an equation of state. An equation of state in the form (3) still holds separately from the vapor pressure formula and says something different from the latter.

Phase changes are driven by the addition or subtraction of heat by some external agent. On a cooktop, a flame at about 1900°C, delivers heat to boiling water at 100°C. At one atmosphere and 100°C, the evaporation of each mole of water requires a fixed amount of heat, the “molar heat of vaporization”. This quantity is commonly denoted ΔH . We will use somewhat unorthodox units so as to simplify the work of students in this course. At 1 atmosphere and 100°C,

$$\Delta H = 401.3 \text{ liter} - \text{atmospheres per mole}$$

⁶Heat capacities are commonly measured in Joules per mole per degree K. Heat is a form of energy, which has a multiplicity of choices for units. Mechanical work is another kind of energy and eventually, a “natural” unit for mechanical work, the liter-atmosphere, has to be made convertible to the SI unit for heat, the Joule(J).

⁷Phase changes are so simple that many chemists would refuse to call them chemical reactions.

⁸This phase change does not violate IV=DP because there is a drastic change in the volume, not just a small perturbation.

⁹Of course, the two molar volumes may differ.

¹⁰This linkage is the simplest illustration of the Gibbs “phase rule”.

¹¹The vapor pressure, $p_{\text{vp}}(T)$, is also called the saturation pressure at T .

In more interesting situations, a liquid *solution* of two or more substances can also be in equilibrium with a mix of vapors of those same substances. Then the (total) vapor pressure of the solution will depend not only on temperature, as in (VP), but also on the composition of the solution.¹²

¹²If there are n_1 moles of one liquid and n_2 moles of a second liquid in a liquid solution of volume V , the total vapor pressure is now an intensive function of n_1 , n_2 and V .