Introduction to Physical Chemistry – Lecture 3

I. LECTURE OVERVIEW

In this lecture, we will discuss more general equations of state than just the Ideal Gas Law.

II. A QUICK NOTE ON PARTIAL PRESSURES

The concept of *partial pressure* is applied to mixtures of gases. Consider two gases, A and B, in some box, at a total pressure P. If there are n_A moles of the first gas, and n_B moles of the second, then the total number of moles is $n = n_A + n_B$, and the *mole fraction* of A is $x_A = n_A/n$, and the mole fraction of B is $x_B = n_B/n$.

We then define the partial pressure of A to be $p_A = x_A P$, and the partial pressure of B to be $p_B = x_B P$. More generally, if a gas is composed of a mixture of n_1 moles of substance 1, n_2 moles of substance 2, etc., then the partial pressure of substance i is given by $p_i = x_i P$, where $x_i = n_i/(n_1 + n_2 + \cdots + n_N)$ is the mole fraction of substance i.

For an ideal gas, the partial pressure is a physical quantity, in that it gives the pressure of that gas in the system. To see this, note from the ideal gas law that,

$$p_i = \frac{n_i RT}{V} \tag{1}$$

while if n is the total number of moles in the system, then,

$$P = \frac{nRT}{V} \tag{2}$$

so that $p_i/P = n_i/n = x_i$.

For real gases, however, intermolecular interactions means that the total pressure is not the sum of the partial pressures. This is a complicated issue, though, and we will deal with it a bit later.

III. TWO ADDITIONAL MEASURES OF PRESSURE

We should introduce two measures of pressure that we did not cover in the previous two lectures: The Torr and mmHg.

The Torr is defined as 1/760 atm. The mmHg is the amount of pressure exerted by a column of mercury 1 mm high. It turns out that 1 Torr is almost exactly equal to 1 mmHg.

As an exercise, we can compute the density of mercury based on the information given. We know that, to a good approximation, a column of mercury 760 mm high exerts a pressure of 1 atm = 101,325 Pa at its base. For a fluid of constant density, we have $P = \rho g h$, where ρ is the density of the substance. Therefore,

$$\rho = \frac{P}{gh} \Rightarrow$$

$$\rho_{mercury} = \frac{101,325 N/m^2}{9.8 m/s^2 \times 0.76 m} =$$

$$13,604 \frac{kgm}{s^2} \frac{s^2}{m^4} = 13,604 kg/m^3 =$$

$$13,604 \frac{kg}{m^3} \frac{1000g}{kg} \frac{1m^3}{10^6 cm^3} = 13.604 g/cm^3 \tag{3}$$

and so the density of mercury is 13.604 grams per milliliter.

IV. EQUATIONS OF STATE AND REAL GASES

A. What is an equation of state?

The Ideal Gas Law is what is known as an *Equation of State*. That is, it provides a relation between various thermodynamic variables associated with the gas. In our case, the Ideal Gas Law relates the pressure P, volume V, temperature T, and number of moles n to one another in a closed form expression.

For real gases, the ideal gas law will generally not hold. This is due to the fact that molecules are not point-particles, but in fact occupy space. Secondly, and more importantly, the particles constituting a gas will generally interact with each other. The stronger these intermolecular interactions, the more the behavior of the gas will deviate from the ideal gas law.

B. Compression factor

One way to measure the deviation of a gas from ideal gas behavior is via a *compression factor*, denoted Z. If we let $\bar{V} = V/n$ denote the specific volume of a gas (the volume per mole of gas), then the ideal gas law reads,

$$p\bar{V} = RT \tag{4}$$

If we define,

$$Z = \frac{p\bar{V}}{RT} \tag{5}$$

then $Z = 1$ for an ideal gas. Therefore, deviations from Z may be used to measure deviation from ideal gas behavior.

C. Virial equations of state

Now, at a given temperature, and for a given number of moles, we expect that the pressure uniquely specifies the specific volume (as the pressure increases, the density increases and hence the specific volume decreases). Therefore, $\bar{V} = \bar{V}(p, T)$, so that $Z = p\bar{V}(p, T)/(RT) = Z(p, T)$ (that is, at a given temperature T, specifying p uniquely determines Z).

We can now expand Z in a Taylor series in p, to obtain,

$$Z(p, T) = 1 + B_1(T)p + B_2(T)p^2 + \ldots \qquad (6)$$

where the first term is 1 because as $p \to 0$, we expect to recover ideal gas behavior, so that $Z \to 1$.

But this gives,

$$p\bar{V} = RT(1 + B_1(T)p + B_2(T)p^2 + \ldots) \qquad (7)$$

which is known as a *virial equation of state*. The terms B_1, B_2, etc. are known as *virial coefficients* of the gas.

An alternative form of the virial expansion is to consider pressure as a function of specific volume. Instead of writing an expression $p = p(\bar{V}, T)$, however, we write $p = p(1/\bar{V}, T)$. The reason for this is that we want the first term in our virial expansion to be 1. As $1/\bar{V} \to 0$, we have that $\bar{V} \to \infty$, which means that the specific volume is becoming infinitely large. Physically, this corresponds to a highly dilute gas with large intermolecular distances. Such a gas is expected to behave ideally.

Therefore, following the same reasoning as before, we have $Z = Z(1/\bar{V}, T)$, giving,

$$P\bar{V} = RT(1 + C_1(T)/\bar{V} + C_2(T)/\bar{V}^2 + \ldots) \qquad (8)$$

D. Van der waals equation of state

One of the earliest attempts to modify the ideal gas equation of state to account for the properties of real gases was done by van der Waals. Van der Waals sought to incorporate two effects into an equation of state: (1) The fact that gas molecules are not point particles, but take up space themselves. (2) The additional fact that gas molecules generally exert weak attractive forces on one another at long distances.

If we start with the ideal gas equation of state in the following form,

$$P = \frac{nRT}{V} \qquad (9)$$

then the van der Waals equation may be derived as follows: We let b denote the *molar volume* of the gas, that is, the total amount of space that a mole of gas particles occupy themselves. Then the volume that the gas actually has available is not V, rather it is $V - nb$. So the first modification to the ideal gas law is to replace V in the previous equation with $V - nb$. This gives,

$$P = \frac{nRT}{V - nb} = \frac{RT}{\bar{V} - b} \qquad (10)$$

To account for intermolecular interactions, we note that the pressure acting on the walls of the container depends on both the frequency of collisions of gas particles with the walls, and on the strength of the individual collisions. Each effect is roughly proportional to the molar concentration n/V, so the overall pressure is reduced by an amount proportional to the square of the molar concentration. The final equation of state is then,

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \qquad (11)$$

The van der Waals equation of state may be re-arranged into the following form:

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT \qquad (12)$$

The quantity $a\frac{n^2}{V^2}$ is known as the *internal pressure* of the gas.

Note that when the temperature is high, the term $-a/\bar{V}^2$ in the van der Waals equation may be neglected. Furthermore, when the concentration of gas molecules is low, so that $\bar{V}$ is large, then the molar volume b can be neglected, giving the ideal gas equation of state. Therefore, the van der Waals equation reduces to the ideal gas equation of state under the appropriate conditions.

We will come back to this equation a little bit later.

E. Critical constants

When a gas is cooled at constant pressure, its density increases, and its specific volume decreases. The average energy of the gas particles also decreases, so that the gas particles move more slowly. Eventually, the specific volume of the gas reaches a point where the distances between the gas particles are sufficiently small, and the energy of the gas particles is sufficiently low, that the gas particles become bound in multimolecular associations with one another. At this point the gas is no longer a gas, but rather has either condensed into a liquid or solid. Such a transformation is known as a *phase transition*.

At the temperature where condensation occurs, say into a liquid, the gas and liquid phases are in equilibrium. Due to intermolecular interactions (collisions, long-range forces), some of the molecules in the liquid state will invariably enter the gas phase. Thus, the liquid has a certain *vapor pressure* at the given temperature, which is simply the pressure of the gas with which the liquid is in thermodynamic equilibrium.

The *boiling point* of a liquid at a given external pressure is simply the temperature at which the vapor pressure of the liquid is equal to the external pressure. The external gas pressure is no longer sufficiently strong to keep the molecules in the liquid state, and the molecules simply push outward against the external pressure source and enter the gas phase.

Let us now try a different approach to achieving gas-liquid transitions. Instead of cooling a gas at constant

pressure, let us compress it at constant temperature. Eventually, the pressure will equal the vapor pressure of the gas at the given temperature, and the gas will liquefy. Basically, the gas molecules become compressed sufficiently close together that the intermolecular attractions become sufficiently strong to produce a phase transition into a bound, liquid state.

Let us consider this liquification process as a function of temperature. For every temperature T, there is a critical pressure $P_{vl}(T)$ at which the vapor to liquid transition takes place. At this boundary, the liquid and gas states are characterized by different densities, or equivalently, specific volumes. The gas has a specific volume $\bar{V}_g = \bar{V}_g(T, P_{vl}(T))$, while the liquid has a specific volume $\bar{V}_l = \bar{V}_l(T, P_{vl}(T))$. Clearly, $\bar{V}_l < \bar{V}_g$.

Now, as we increase the temperature, the gas particles will have more energy, hence a greater pressure will be required to force them together into the liquid state. This means that P_{vl} is an increasing function of T. Furthermore, we expect that, since the gas particles have more energy with increasing temperature, they will on average have to be forced closer together to induce a gas to liquid transition. Therefore, we expect $\bar{V}_g(T, P_{vl}(T))$ to decrease with increasing temperature.

We also expect $\bar{V}_l(T, P_{vl}(T))$ to increase with increasing temperature, since increasing pressure should have only a weak effect on liquid density, but increasing temperature increases the average thermal motions of the liquid molecules, and hence leads to a reduction in density.

Eventually, we will reach a temperature, denoted T_c, at which $\bar{V}_g(T_c, P_{vl}(T_c)) = \bar{V}_l(T_c, P_{vl}(T_c))$. At this temperature, the densities of the liquid and gas phases are identical. Therefore, compressing the gas at this temperature leads to no discernible phase transition. At temperatures $T > T_c$, the gas is so hot that to liquefy it would require compressing the gas to an extent that would make the "gaseous" state more dense than the "liquid" state. Clearly, this makes no sense, so that at temperatures greater than T_c, there is no distinction between gas and liquid, and no gas-liquid phase transition is observed. A gas in this temperature regime is known as *supercritical*.

Given T_c, we can define $P_c = P_{vl}(T_c)$, and $\bar{V}_c = \bar{V}_g(T_c, P_{vl}(T_c)) = \bar{V}_l(T_c, P_{vl}(T_c))$.

We should point out that gases such as oxygen, nitrogen, and hydrogen are supercritical at room temperature. That is why these gases cannot be liquefied by compressing them at room temperature. They must first be cooled, then compressed.

F. Critical constants in the van der Waals equation

The van der Waals equation is interesting because it predicts vapor-liquid equilibria, in contrast to the ideal gas law. We illustrate what we mean: Writing the van
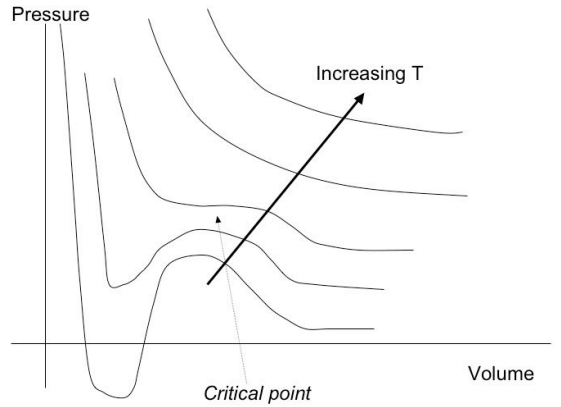

FIG. 1: Illustration of the van der Waals isotherms.

der Waals equation in the form,

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \qquad (13)$$

we can plot P as a function of $\bar{V}$ for various temperatures (see Figure 1). At high temperatures, the term $-a/\bar{V}^2$ is negligible, and we essentially have the ideal gas law, modified slightly by the presence of the molar volume term b. At high $\bar{V}$, however, this term may also be neglected.

At lower temperatures, the term $-a/\bar{V}^2$ is no longer negligible. Because this function increases from $-\infty$ at $\bar{V} = 0$ to 0 as $\bar{V} \to \infty$, and because $RT/(\bar{V} - b)$ decreases from ∞ at $\bar{V} = b$ to 0 as $\bar{V} \to \infty$, then at lower temperatures P first decreases to a local minimum as a function of $\bar{V}$, increases to a local maximum, and then decreases steadily to 0.

If we let $\bar{V}_{min}$ denote where the locally minimum pressure, P_{min} is attained, and $\bar{V}_{max}$ denote where the locally maximum pressure, P_{max} is attained, then the region between $\bar{V}_{min}$ and $\bar{V}_{max}$ is physically unrealizable. This is because it is a region where the specific volume and pressure are both increasing, while physically we must have that the specific volume decreases as pressure increases.

The region between P_{min} and P_{max}, with $P > 0$, is interesting because there are three distinct specific volumes $\bar{V}$ giving rise to the given pressure P. One of these, as we have seen, lies in the physically unrealizable region. However, for a $P > 0, P_{min}, P < P_{max}$, there exists a $\bar{V}_1 < \bar{V}_{min}$ for which $P = P(\bar{V}_1)$, where $P(\bar{V}_1)$ is evaluated using the van der Waals equation. This is because $P(\bar{V})$ is decreasing from ∞ to P_{min} as $\bar{V}$ increases from b to $\bar{V}_{min}$. Also, there exists a $\bar{V}_2 > \bar{V}_{max}$ for which $P = P(\bar{V}_2)$. This is because $P(\bar{V})$ is decreasing from P_{max} to 0 as $\bar{V}$ increases from $\bar{V}_{max}$ to ∞.

The two physically realizable solutions $\bar{V}_1 < \bar{V}_2$ in the region known as the *van der Waals loops*, corresponds to a vapor-liquid equilibrium. We see then how, at sufficiently low temperatures, the van der Waals equation gives rise to phase transitions.

We know, however, that at sufficiently high temperatures, the van der Waals equation behaves similarly to the ideal gas equation, for which no phase transitions are possible.

The transition from the low temperature behavior of the van der Waals equation to the high temperature behavior must therefore occur by the steady disappearance of the van der Waals loops as the temperature increases. This means that $\bar{V}_{min}$ and $\bar{V}_{max}$ should converge as T approaches T_c. Finally, at T_c, $\bar{V}_{min} = \bar{V}_{max}$, so that this point is neither a local minimum or maximum, but rather a point where *both* $dP/d\bar{V}$ and $d^2P/d\bar{V}^2$ vanish.

Differentiating the van der Waals equation of state twice, we obtain,

$$\frac{dP}{d\bar{V}} = -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3}$$

$$\frac{d^2P}{d\bar{V}^2} = \frac{2RT}{(\bar{V} - b)^3} - \frac{6a}{\bar{V}^4} \tag{14}$$

Setting both derivatives equal to 0 and solving, we obtain, $\bar{V} = 3b$, $T = 8a/(27bR)$, and $P = a/(27b^2)$, and so,

$$\bar{V}_c = 3b$$
$$T_c = \frac{8a}{27bR}$$
$$P_c = \frac{a}{27b^2} \tag{15}$$

Of course, different equations of state will yield different values for the critical constants.

In concluding this subsection, we should point out that the van der Waals equation gives a value of $3/8 = 0.375$ for the *critical compression factor*, defined by $Z_c = p_cV_c/(RT_c)$. This value turns out to be somewhat larger than what is measured for a variety of real gases. Nevertheless, it turns out that Z_c is fairly constant at around 0.3 for many gases. This certainly suggests that the van der Waals equation captures key physical properties associated with real gases.

G. The law of corresponding states

The law of corresponding states is a misnomer, in that it is not a derivable law, but rather an educated guess, backed by experiment, that approximates the behavior of real gases.

The idea is as follows: Different gases will generally have different values of T_c, P_c, and $\bar{V}_c$. This follows from the different characteristic particle sizes and strength of the interparticle interactions. However, for a given gas, we can define reduced variables as follows: At a temperature T, define $T_r = T/T_c$. The reduced variables P_r and $\bar{V}_r$ are defined similarly.

The law of corresponding states then argues that there is a universal equation of state for real gases when the equation of state is expressed in terms of the reduced variables. In other words, two gases at the same reduced temperature and volume will have the same reduced pressure.

Intuitively, the motivation for this hypothesis is that two gases with the same set of reduced variables have an equal level of deviation from ideal gas behavior. The idea is that the values of the critical constants set up natural "length" scales characterizing the behavior of the gas. Rescaling the parameters associated with the gas in terms of these natural length scales gives a set of dimensionless parameters that effectively hides these "length" scales. Therefore, it is not unreasonable to assume that real gases may exhibit universal behavior when expressed in terms of the reduced variables.

In reality, the law of corresponding states only works for gases composed of spherical, non-polar molecules. For non-spherical or polar molecules, the principle fails, sometimes badly.

V. AN ALTERNATE DERIVATION OF THE VAN DER WAALS EQUATION

We conclude this lecture by providing a plausible, alternative derivation to the van der Waals equation of state. The idea is as follows: Because of intermolecular interactions, the individual gas particles, denoted A, may form transient pairwise associations with one another, so that the gas may be regarded as a chemically reacting system with the pair of chemical reactions,

$$A + A \rightarrow A_2$$
$$A_2 \rightarrow A + A \tag{16}$$

where the first reaction has a second-order rate constant of k_f, and the second reaction has a first-order rate constant of k_r. We then have,

$$\frac{d[A]}{dt} = -k_f[A]^2 + 2k_r[A_2]$$

$$\frac{d[A_2]}{dt} = \frac{1}{2}k_f[A]^2 - k_r[A_2] \tag{17}$$

At steady-state, we have $k_f[A]^2 = 2k_r[A_2]$, so that $2[A_2]/[A]^2 = K \equiv k_f/k_r$.

Now, the total concentration of gas particles A is given by $[A] + 2[A_2]$. By conservation of mass, this quantity is a constant, given by $[A]_0$. We therefore have that,

$$\frac{[A]_0 - [A]}{[A]^2} = K \tag{18}$$

Now, define $x = [A]_0 - [A]$, so that $[A] = [A]_0 - x$. Then, x is the solution to the quadratic,

$$0 = x^2 - (2[A]_0 + 1/K)x + [A]_0^2 \tag{19}$$

so that,

$$x = [A]_0 + \frac{1}{2K}(1 - \sqrt{1 + 4K[A]_0}) \tag{20}$$

where the alternative solution is not realistic since it gives $x > [A]_0$.

Now, we are ultimately considering a gas with *weak* intermolecular interactions. Therefore, the steady-state concentration of particle-pairs A_2 should be small, which means that K is small. This allows us to Taylor-expand the square root term out to second-order in K, giving,

$$\sqrt{1 + 4K[A]_0} \approx 1 + 2K[A]_0 - 2K^2[A]_0^2 \qquad (21)$$

so that,

$$x \approx K[A]_0^2 \qquad (22)$$

The total concentration of particles is then,

$$
\begin{aligned}
[A] + [A_2] &= [A]_0 - ([A]_0 - [A]) + \frac{1}{2}2[A_2] \\
&= [A]_0 - ([A]_0 - [A]) + \frac{1}{2}([A]_0 - [A]) \\
&= [A]_0 - \frac{1}{2}([A]_0 - [A]) \\
&= [A]_0 - \frac{K}{2}[A]_0^2 \qquad (23)
\end{aligned}
$$

Therefore, intermolecular interactions have reduced the effective molar concentration $[A]_0 = n/V$ of gas particles by an amount $(K/2)(n/V)^2$.

Applying the ideal gas law using this reduced molar concentration, we obtain,

$$P = \frac{nRT}{V} - \frac{RTK}{2}\left(\frac{n}{V}\right)^2 \qquad (24)$$

The introduction of the factor b has been discussed previously. Clearly, in this case, we have $a = RTK/2$.