

# Chapter 5

## Gasses

### 5.1 Ideal Gas Law

In 1662, Robert Boyle published the results of his experiments showing that the pressure of a gas is inversely proportional to its volume ( $P \propto \frac{1}{V}$ ). About 100 years later, Jacques Charles showed that gases tend to expand when heated. This was subsequently interpreted as the volume of a gas being directly proportional to its temperature ( $V \propto T$ ). Near the beginning of the 19th century, Joseph Gay-Lussac published the results of his experiments showing that the pressure of a gas is directly proportional to its temperature. Finally, also in the early 1800s, Amedeo Avogadro hypothesized that the volume of a gas was directly proportional to the “amount of substance” of the gas. When combined together, these empirical results are referred to as the ideal gas law.

$$PV = nRT \quad (5.1)$$

The variable  $n$  in Equation 5.1 is the number of moles of the gas and the variable  $R = 8.314 \frac{\text{J}}{\text{Kmol}}$  is the ideal gas constant, which is also commonly referred to as the molar gas constant. We can relate the number of moles of the gas ( $n$ ) and the number of molecules of the gas, denoted as  $N$ , with the Avogadro constant ( $N_A$ ).

$$n = \frac{N}{N_A} \rightarrow PV = \frac{N}{N_A}RT \rightarrow PV = N \left( \frac{R}{N_A} \right) T$$

The parenthetical term in this equation is usually expressed as the constant  $k_B$ , which is called the Boltzmann constant.

$$k_B = \frac{R}{N_A} \rightarrow k_B = \frac{8.3145 \frac{\text{J}}{\text{Kmol}}}{6.022 \times 10^{23} \frac{1}{\text{mol}}} \rightarrow k_B = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

$$PV = Nk_B T \quad (5.2)$$

At this point, it is important to make clear what is meant by *ideal* in the ideal gas law. A gas can be considered to be ideal if the molecules of the gas possess only kinetic energy and there is no potential energy associated with the interaction between the molecules of the gas; the molecules of the gas can exchange kinetic energy and momentum with one another through collisions. These conditions can often be approximately obtained by working with gases at low concentrations, especially monotonic gases (to avoid worrying about rotational kinetic energy and angular momentum).

The focus of this chapter is on *classical* gasses consisting of indistinguishable molecules. In other words, the gasses discussed here are described by Maxwell-Boltzmann statistics. We will return to a discussion of *quantum* gasses later.

## 5.2 Partition Function

A system of classical and indistinguishable molecules would be described by Maxwell-Boltzmann statistics. Thus, the partition function for this system can be determined using Equation 4.8.

$$Z = \left( \frac{e}{Nh^3} \right)^N \int e^{-\beta \sum_{i=1}^N H(\vec{q}_i, \vec{p}_i)} d^3\vec{p}_1 d^3\vec{p}_2 \cdots d^3\vec{p}_N d^3\vec{q}_1 d^3\vec{q}_2 \cdots d^3\vec{q}_N$$

Let's now split the Hamiltonian into two components - one for the kinetic energy, denoted as  $Z_K$ , which depends on momentum but not position, and one for the potential energy, denoted by  $Z_U$ , which depends on position but not momentum.

$$Z = \left( \frac{e}{Nh^3} \right)^N Z_K Z_U$$

Where,

$$Z_K = \int e^{-\beta K(p_1, p_2, \dots, p_N)} d^3\vec{p}_1 d^3\vec{p}_2 \cdots d^3\vec{p}_N$$

$$Z_U = \int e^{-\beta U(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)} d^3\vec{q}_1 d^3\vec{q}_2 \cdots d^3\vec{q}_N$$

Let's now calculate the partition function for an ideal gas and for a real gas.

### 5.2.1 Ideal Gas

The Hamiltonian for an ideal gas is a function of only the kinetic energy of the gas molecules.

$$K = \left( \frac{1}{2m} \right) \sum_{i=1}^N p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2 \quad U = 0$$

Let's first calculate  $Z_K$ .

$$Z_K = \int e^{-\frac{\beta}{2m} \sum_{i=1}^N p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2} d^3\vec{p}_1 d^3\vec{p}_2 \cdots d^3\vec{p}_N$$

The integration can be made simpler by changing the coordinates (Section A.1).

$$Z_K = \int e^{-\beta \sum_{i=1}^N p_i^2} \left( \prod_{i=1}^N 4\pi p_i^2 dp_i \right)$$

Since all the integrals are identical, we can combine them into a single integration.

$$Z_K = \left( \int_0^\infty e^{-\frac{\beta p^2}{2m}} 4\pi p^2 dp \right)^N$$

$$Z_K = \left[ 2\sqrt{2} \left( \frac{m\pi}{\beta} \right)^{\frac{3}{2}} \right]^N \rightarrow Z_K = \left( \frac{2m\pi}{\beta} \right)^{\frac{3N}{2}}$$

Next, let's determine  $Z_U$ .

$$Z_U = \left( \int e^0 d^3\vec{q}_1 \cdots d^3\vec{q}_N \right) = \left( \int d^3\vec{q}_1 \right) \left( \int d^3\vec{q}_2 \right) \cdots \left( \int d^3\vec{q}_N \right)$$

Each of these integrals is over all possible positions accessible to the molecules and is thus equal to the volume of the gas.

$$Z_U = (V)(V) \cdots (V) = V^N$$

Thus,

$$Z = \left( \frac{e}{N h^3} \right)^N \left( \frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} V^N$$

$$Z = \left[ \left( \frac{eV}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right]^N \quad (5.3)$$

If the molecules of the gas were distinguishable, the partition function would be

$$Z = \left[ V \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right]^N \quad (5.4)$$

### Gravitational Potential Energy

If we allow the molecules of the gas to interact with an external gravitational field. Let's assume that the container holding the gas is located on the surface of the Earth and has a height  $H$ . We will further assume that the Earth's gravitational field is directed along the  $z$ -axis. If we still do not allow the molecules of the gas to interact with one another, we can calculate  $Z_U$  as

$$Z_U = \left( \int_0^H e^{-\beta mgz} dz \int dx dy \right)^N$$

The variable  $g$  denotes the magnitude of the Earth's gravitational field at the location of the container. The integral over  $dx$  and  $dy$  are the cross-sectional area of the container holding the gas, which we can denote as  $A$ .

$$Z_U = A^N \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right)^N$$

The partition function for the gas is thus

$$Z = \left( \frac{eA}{N h^3} \right)^N \left( \frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right)^N$$

### 5.2.2 Real Gas

Let's consider a gas consisting of  $N$  indistinguishable molecules which have both kinetic and potential energies; in other words, the Hamiltonian for this system consists of both kinetic and potential energy terms. The calculation of  $Z_K$  is identical to that for an ideal gas.

$$Z_K = \left( \frac{2m\pi}{\beta} \right)^{\frac{3N}{2}}$$

The calculation of  $Z_U$  is different, however, as the real gas has a non-zero potential energy associated with the interactions between its molecules. Several approaches can be used to calculate the potential energy contribution to the partition function of a real gas. We will focus on the *mean field approximation* approach and apply it to the specific example of a Van der Waals gas.

#### Van der Waals Gas

A Van der Waals gas is a canonical example of model for real gasses. There are many versions of the potential energy used for a Van der Waals gas, but we will use the following:

$$u(r) = \begin{cases} \infty & r < r_0 \\ -u_0 \left( \frac{r_0}{r} \right)^n & r > r_0 \end{cases}$$

The variables  $u_0$  and  $r_0$  in this equation are constants, with  $r_0$  reflecting the finite size of a molecule of the gas and  $u_0$  parameterizing the potential energy associated with the interaction between the molecules. Notice that we are explicitly modeling this interaction as attractive since we are associating it with a negative potential energy. This net attractive interaction is frequently associated with the electric dipoles of the molecules, including those involving induced dipoles.

### Mean Field Approximation

We argue that the other molecules of the gas surrounding any particular molecule form an almost continuous distribution or continuum of molecules, whose positions can be approximately assumed to be unperturbed by the presence of our particular molecule of focus. In this approximation, we model our particular molecule moving through the *mean field* created by this continuous cloud of other molecules and thus the potential energy depends on the position of the particular molecule only, and not on a summation of pairwise interactions. The gas can then be modeled as an ensemble of independent molecules moving through this mean field.

The total potential energy of the system of  $N$  molecules of gas is thus

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i=1}^N u_{eff}(\vec{r}_i)$$

In this equation, the variable  $u_{eff}(\vec{r}_i)$  denotes the effective potential energy of the  $i^{\text{th}}$  molecule of the gas located at  $\vec{r}_i$ . The partition function for the system is thus

$$Z_U = \left[ \int e^{-\beta u_{eff}(\vec{r})} d^3\vec{r} \right]^N$$

In the case that the molecules of the gas are uniformly distributed throughout the system, the effective potential energy should not depend on position, but rather be a constant. In other words, there should be an effective potential that is constant over the entire volume of the system. We would anticipate, however, that this approximation would break down when the distance between molecules is close to the size of a molecule. More specifically, for these short separation distances, we would expect a large repulsive force would act between molecules of the gas for the simple fact that the molecules have finite size and cannot occupy the same location in the gas<sup>1</sup>. We could model these short range interactions as a reduction in the accessible volume of the gas.

If the radius of a molecule is  $R_0$ , the volume excluded by any molecule<sup>2</sup> is  $\frac{4}{3}\pi(2R_0)^3$ . As there are  $\frac{1}{2}N(N-1)$  pairs of molecules, the total excluded volume can be modeled as

<sup>1</sup>We could also conjure up other repulsive interactions, such as electrostatic interactions, that could contribute to this repulsion

<sup>2</sup>The closest separation between any two molecules is twice the radius of a molecule

$$\frac{1}{2}N(N-1)\left(\frac{4}{3}\pi(2R_0)^3\right) \approx \frac{2}{3}\pi N^2 r_0^3$$

The variable  $r_0 = 2R_0$  denotes the distance of closest approach between any two molecules. The excluded volume per particle is thus

$$V_0 = \frac{\frac{2}{3}\pi N^2 r_0^3}{N} \rightarrow V_0 = \frac{2}{3}\pi N r_0^3 \rightarrow V_0 = bN$$

The variable  $b = \frac{2}{3}\pi r_0^3$  can be thought of as a measure of the volume associated with a single particle of the gas. We can now approximate the integral in the partition function as

$$\int e^{-\beta u_{eff}(\vec{r})} d^3\vec{r} = (V - V_0) e^{-\beta u_{eff,0}}$$

The variable  $u_{eff,0}$  is constant and corresponds to the mean value of the effective potential energy of the interactions between the molecules of the gas. We would expect this term to depend on the density of the gas and thus that it could be expressed as a power series in the density ( $\frac{N}{V}$ ) of the gas.

$$u_{eff,0} = C_0 + C_1 \left(\frac{N}{V}\right) + C_2 \left(\frac{N}{V}\right)^2 + \dots$$

$$u_{eff,0} = \sum_{i=0}^{\infty} C_i \left(\frac{N}{V}\right)^i$$

For an ideal gas,  $C_i = 0$  for all  $i$ . For a Van der Waals gas, we typically set  $C_1 = -a$  and  $C_{i \neq 1} = 0$ . The negative sign for  $C_1$  reflects that the interaction between molecules in the Van der Waals gas favors the molecules being closer together. In other words, it is an attractive potential. Thus, for the Van der Waals gas we have

$$u_{eff,0} = -a \frac{N}{V}$$

The variable  $a$  in this expression is positive and depends on the gas. Putting this all together gives us

$$\begin{aligned} Z &= \left[ \left(\frac{e}{N}\right) \left(\frac{2m\pi}{\beta h^2}\right)^{\frac{3}{2}} \right]^N \left[ (V - bN) e^{\beta a \frac{N}{V}} \right]^N \\ Z &= \left(\frac{Ve}{N}\right)^N \left(\frac{2m\pi}{\beta h^2}\right)^{\frac{3N}{2}} \left[ \left(1 - \frac{bN}{V}\right) e^{\beta a \frac{N}{V}} \right]^N \end{aligned} \quad (5.5)$$

We see that the partition function for the Van der Waals gas is equal to the partition function for an ideal gas (Equation 5.3) multiplied by a corrective term.

### 5.3 Mean Energy

We can use Equation 4.1 to determine the equation for the mean energy of the gas.

#### Ideal Gas

The mean energy of an ideal gas is the same regardless of whether the molecules are distinguishable or indistinguishable.

$$\begin{aligned}\bar{E} &= -\frac{\partial}{\partial\beta} \ln \left( \left[ \left( \frac{eV}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right]^N \right) \\ \bar{E} &= -N \frac{\partial}{\partial\beta} \left[ \ln \left( \left( \frac{eV}{N} \right) \left( \frac{2m\pi}{h^2} \right)^{\frac{3}{2}} \right) - \frac{3}{2} \ln(\beta) \right] \\ \bar{E} &= -N \left[ -\frac{3}{2} \frac{1}{\beta} \right] = \frac{3N}{2\beta}\end{aligned}$$

This result is also consistent with our expectations from the equipartition theorem. It further provides additional motivation for a conceptual understanding of  $\beta$  as a measure of average energy.

$$\bar{E} = \frac{3}{2} \frac{N}{\beta} \quad \rightarrow \quad \beta = \frac{3}{2} \frac{N}{\bar{E}}$$

Specifically,  $\beta$  is inversely proportional to the average energy of the system.

#### Gravitational Potential Energy

$$\begin{aligned}\bar{E} &= -\frac{\partial}{\partial\beta} \ln \left[ \left( \frac{eA}{Nh^3} \right)^N \left( \frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right)^N \right] \\ \bar{E} &= -N \frac{\partial}{\partial\beta} \left[ \ln \left( \left( \frac{eA}{N} \right) \left( \frac{2m\pi}{h} \right)^{\frac{3}{2}} \right) - \frac{3}{2} \ln(\beta) + \ln \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right) \right] \\ \bar{E} &= -N \left[ -\frac{3}{2} \frac{1}{\beta} + \frac{e^{\beta mgH}}{\beta^2 mg} (1 + \beta mgH - e^{-\beta mgH}) \right] \\ \bar{E} &= N \left[ \frac{5}{2\beta} - \frac{mgH}{e^{\beta mgH} - 1} \right]\end{aligned}$$

This equation is identical to the previously derived expression for the mean energy of an ideal gas when  $g = 0$ , as expected.

**Van der Waals Gas**

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln \left[ \left( \frac{Ve}{N} \right)^N \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3N}{2}} \left[ \left( 1 - \frac{bN}{V} \right) e^{\beta a \frac{N}{V}} \right]^N \right]$$

$$\bar{E} = -N \frac{\partial}{\partial \beta} \left( \ln \left[ \left( \frac{Ve}{N} \right) \left( \frac{2m\pi}{h^2} \right)^{\frac{3}{2}} \left( 1 - \frac{bN}{V} \right) \right] - \frac{3}{2} \ln(\beta) + \beta a \frac{N}{V} \right)$$

$$\bar{E} = \frac{3}{2} \frac{N}{\beta} - \frac{aN^2}{V} \rightarrow \bar{E} = N \left( \frac{3}{2\beta} - a \frac{N}{V} \right)$$

As expected, this is the average energy of an ideal gas with a correction term reflecting interactions between the molecules. This correction term is negative as the presence of an attractive interaction (*i.e.*, a negative potential energy) will decrease the overall energy of the system.

**5.4 Entropy**

We can use Equation 4.3 to determine the equation for the entropy of the gas.

**Ideal Gas**

$$\mathcal{S} = \ln \left( \left( \frac{Ve}{N} \right)^N \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3N}{2}} \right) + \beta \left( \frac{3}{2} \frac{N}{\beta} \right)$$

$$\mathcal{S} = \ln \left( \left( \frac{Ve}{N} \right)^N \right) + \ln \left( \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3N}{2}} \right) + \beta \left( \frac{3}{2} \frac{N}{\beta} \right)$$

$$\mathcal{S} = \ln \left( \left( \frac{V}{N} \right)^N \right) + \ln \left( (e)^N \right) + \ln \left( \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3N}{2}} \right) + \beta \left( \frac{3}{2} \frac{N}{\beta} \right)$$

$$\mathcal{S} = N \ln \left( \frac{V}{N} \right) + N \ln(e) + N \ln \left( \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right) + \beta \left( \frac{3}{2} \frac{N}{\beta} \right)$$

$$\mathcal{S} = N \left[ \ln \left( \frac{V}{N} \right) + 1 + \ln \left( \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right) + \frac{3}{2} \right]$$

$$\mathcal{S} = N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \quad (5.6)$$



**Gravitational Potential Energy**

$$\mathcal{S} = \ln \left[ \left( \frac{eA}{Nh^3} \right)^N \left( \frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right)^N \right] + \beta N \left[ \frac{5}{2\beta} - \frac{mgH}{e^{\beta mgH} - 1} \right]$$

$$\mathcal{S} = N \left[ \ln \left[ \left( \frac{eA}{N} \right) \left( \frac{2m\pi}{h^2\beta} \right)^{\frac{3}{2}} \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right) \right] + \frac{5}{2} - \frac{\beta mgH}{e^{\beta mgH} - 1} \right]$$

$$\mathcal{S} = N \left[ \ln \left[ \left( \frac{A}{N} \right) \left( \frac{2m\pi}{h^2\beta} \right)^{\frac{3}{2}} \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right) \right] + \frac{7}{2} - \frac{\beta mgH}{e^{\beta mgH} - 1} \right]$$

$$\begin{aligned} \mathcal{S} = N \left[ \ln \left( \frac{A}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{h^2\beta} \right) + \frac{7}{2} \right] + \\ N \left[ \ln \left( \frac{1 - e^{-\beta mgH}}{\beta gm} \right) - \frac{\beta mgH}{e^{\beta mgH} - 1} \right] \end{aligned}$$

**Van der Waals Gas**

$$\begin{aligned} \mathcal{S} = N \left[ \ln \left( \frac{V}{N} \right) + 1 + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \ln \left( 1 - \frac{bN}{V} \right) + \beta a \frac{N}{V} \right] + \\ N\beta \left( N \left( \frac{3}{2\beta} - a \frac{N}{V} \right) \right) \end{aligned}$$

$$\mathcal{S} = N \left[ \ln \left( \frac{V}{N} \right) + 1 + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \ln \left( 1 - \frac{bN}{V} \right) + \frac{3}{2} \right]$$

$$\mathcal{S} = N \left[ \ln \left( \frac{V - bN}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \quad (5.7)$$

The entropy of Van der Waals gas has an effective volume that is smaller than the total volume by the correction factor  $bN$ , which accounts for the finite size of the molecules of the gas. Otherwise, the two expressions for entropy are identical. Interestingly, this means that the entropy of a Van der Waals gas will always be less than the entropy of an ideal gas, when comparing gasses of the same volume and number of molecules.

**5.5 Equation of State**

We can use Equation 3.26 to determine the equation of state of the gas.

**Ideal Gas**

$$\beta P = \left( \frac{\partial}{\partial V} \right)_E \left( N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \right)$$

The equation for the entropy of the gas must be expressed explicitly in terms of the energy  $E$  so that the partial derivative may be taken correctly. For an ideal gas,

$$\overline{E} = \frac{3N}{2\beta} \quad \rightarrow \quad \beta = \frac{3N}{2\overline{E}}$$

Let's now assume that the number of molecules in the gas is so large (*i.e.*, the size of the system is so large) that  $\overline{E} = E$ . Thus,

$$\beta = \frac{3N}{2E}$$

Substitution then gives us

$$\begin{aligned} \beta P &= \left( \frac{\partial}{\partial V} \right)_E \left( N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\frac{3N}{2E} h^2} \right) + \frac{5}{2} \right] \right) \\ \beta P &= \left( \frac{\partial}{\partial V} \right)_E \left( N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{4m\pi E}{3N h^2} \right) + \frac{5}{2} \right] \right) \\ \beta P &= \frac{N}{V} \quad \rightarrow \quad PV = \frac{N}{\beta} \end{aligned} \tag{5.8}$$

Equation 5.8 is the equation of state for an ideal gas. If we once again substitute the expression relating  $\beta$  and  $E$  into Equation 5.8 we have

$$PV = \frac{N}{\frac{3N}{2E}} \quad \rightarrow \quad P = \frac{2E}{3V}$$

Thus, as expected, we can think of the pressure of the gas as a measure of the energy density (*i.e.*, energy per unit volume) of the gas.

**Van der Waals Gas**

$$\beta P = \left( \frac{\partial}{\partial V} \right)_E \left( N \left[ \ln \left( \frac{V - bN}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \right)$$

As before, we need to express the entropy explicitly terms of the energy to calculate the partial derivative. Let's begin this process by writing the expression for entropy as a function of terms that involve  $V$ , terms that involve  $\beta$ , and terms involving other variables.

$$\beta P = \left( \frac{\partial}{\partial V} \right)_E \left( N \left[ \ln \left( \frac{V - bN}{N} \right) + \frac{3}{2} \ln \left( \frac{1}{\beta} \right) + \mathcal{S}_0 \right] \right)$$

where  $\mathcal{S}_0 = \frac{3}{2} \ln \left( \frac{2m\pi}{h^2} \right) + \frac{5}{2}$ . We can now express  $\beta$  in terms of  $E$ .

$$\bar{E} = E = N \left( \frac{3}{2\beta} - a \frac{N}{V} \right) \rightarrow \frac{1}{\beta} = \frac{2E}{3N} + \frac{2aN}{3V}$$

$$\beta P = \left( \frac{\partial}{\partial V} \right)_E \left( N \left[ \ln \left( \frac{V - bN}{N} \right) + \frac{3}{2} \ln \left( \frac{2E}{3N} + \frac{2aN}{3V} \right) + S_0 \right] \right)$$

$$\beta P = \frac{N}{2} \left( -\frac{3}{V} + \frac{2}{V - bN} + \frac{3E}{aN^2 + EV} \right)$$

We can now substitute back the equation for  $E$ .

$$\begin{aligned} \beta P &= \frac{N}{2} \left( -\frac{3}{V} + \frac{2}{V - bN} + \frac{3N \left( \frac{3}{2\beta} - a \frac{N}{V} \right)}{aN^2 + N \left( \frac{3}{2\beta} - a \frac{N}{V} \right) V} \right) \\ \beta P &= \frac{N}{2} \left( -\frac{3}{V} + \frac{2}{V - bN} + \frac{3N \left( \frac{3}{2\beta} - a \frac{N}{V} \right)}{\frac{3NV}{2\beta}} \right) \\ \beta P &= \frac{N}{2} \left( -\frac{3}{V} + \frac{2}{V - bN} + \frac{3}{V} - \frac{2aN\beta}{V^2} \right) \\ \beta P &= \frac{N}{V - bN} - \frac{a\beta N^2}{V^2} \rightarrow \beta \left( P + a \frac{N^2}{V^2} \right) = \frac{N}{V - bN} \\ \left( P + a \frac{N^2}{V^2} \right) (V - bN) &= \frac{N}{\beta} \end{aligned} \tag{5.9}$$

Equation 5.9 differs from Equation 5.8 by a modification of the volume, to account for the finite size of the molecules of a Van der Waals gas, and by a modification of the pressure to account for the potential energy associated with the interaction between molecules of the gas. We can understand this in the context of viewing pressure as a measure of energy density.

## 5.6 Temperature

Comparing Equation 5.8 with Equation 5.2 gives us

$$\begin{aligned} PV &= \frac{N}{\beta} = Nk_B T \\ \frac{1}{\beta} &= k_B T \end{aligned} \tag{5.10}$$

The relationship between  $T$  and  $\beta$  allows us to define the temperature of a system in terms of the entropy of that system.

$$\frac{1}{T} = k_B \left( \frac{\partial S}{\partial E} \right)_V \rightarrow T = \frac{1}{k_B} \left( \frac{\partial E}{\partial S} \right)_V$$

We also can use the equation relating  $\beta$  and  $T$  to determine a different expression for entropy.

$$d\mathcal{S} = \beta dQ \quad \rightarrow \quad d\mathcal{S} = \frac{dQ}{k_B T} \quad \rightarrow \quad k_B d\mathcal{S} = \frac{dQ}{T}$$

The quantity  $k_B \mathcal{S}$  is also referred to as the entropy and will be denoted by the variable  $S$ .

$$S = k_B \mathcal{S} \quad \rightarrow \quad dS = k_B d\mathcal{S} \quad (5.11)$$

$$dS = \frac{dQ}{T} \quad (5.12)$$

Equation 5.12 is one representation of the 2<sup>nd</sup> Law of Thermodynamics. Finally, this means that Equation 3.7 can be expressed as

$$S = k_B \ln \Omega \quad (5.13)$$

We see that while  $\mathcal{S}$  is dimensionless,  $S$  has units of  $\frac{J}{T}$ , which encourages people to think about  $S$  as some form of energy density. I'm not convinced this is especially helpful, but since you will most often see entropy defined this way, you'd better get used to it.

Finally, we see from Equation 3.23 that the parameter  $\beta$  (or, equivalently, the parameter  $T$ ) relates an inexact differential  $dQ$  to an exact differential  $d\mathcal{S}$ . We can therefore consider  $\beta$  to be an integration factor<sup>3</sup>.

### Say What Now?

Sure, one can argue that since temperature (cast either as  $\beta$  or as  $T$ ) is an integration factor since it converts  $dQ$  into  $d\mathcal{S}$  or  $dS$ , but what does that mean exactly? Temperature is a *real* thing, right? There are thermometers and large LED displays outside of banks after all.

Well, at best we can think about temperature as an *empirical* concept. Think about it. Temperature is measured in terms on the equilibrium between two substances, such as the equilibrium of a system and a mercury thermometer. The level of the mercury in the thermometer will change until the mercury and the system are in *thermal* equilibrium. The level of the mercury at this equilibrium is defined as the temperature of the system. This measurement of equilibrium equates to both the system and the mercury having the same value of  $\beta$  so that changes in the entropy of either component (the system or the mercury) of the combined system associated with the exchange of energy (*e.g.*, heat) between the components are equal in magnitude but opposite in sign so that  $d\mathcal{S}_{total} = 0$  for the system for any exchanged heat. We could use a variety of measurements of this equilibrium rather than the level of mercury in a sealed tube.

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<sup>3</sup>See Section A.4

The discomfort, of course, likely lies on a somewhat deeper level. As stated at the start of this section, we think of temperature as being something real - something that we can sense or feel. I sweat when it is hot outside and I wear a coat when it is cold. We also tend to think of temperature in terms of a connection to energy. Something that is at higher temperature is more energetic, for example. That thinking is aligned with the derivation of the equipartition theorem, which shows that the average energy of a molecule is proportional to  $\beta$  and thus to temperature. So, if we wanted, we could run back to this relationship between average energy and temperature, but then we must always remember that this definition applies only to quadratic terms in the system's Hamiltonian. So, in the end, if we want to get general in our thinking, we should consider temperature either to be a measure of how entropy depends on energy ( $\beta = (\frac{\partial S}{\partial E})_V$  or  $\frac{1}{T} = (\frac{\partial S}{\partial E})_V$ ) or an integrating factor that converts  $dQ$  into  $dS$  or  $dS$ . But that's okay.

It really is okay. And the more we think about this, the more we are comfortable with this. Entropy is a function of energy and it is entirely possible that the dependence will not be linear. In other words, it is possible that  $\frac{\partial S}{\partial E}$  will not be a constant. For example, we see from Equation 5.6 that for an ideal gas  $\frac{\partial S}{\partial E} = \frac{3N}{2E}$ , which is not constant. Because of this, the change in entropy associated with the absorption or release of heat will depend on the energy of the system when that process occurs. The same amount of heat absorbed will have a smaller effect on the entropy of the system when the system is at high energy than when the system is at low energy. Intuitively, this kind of makes sense to us if we process the effect of the heat as a fraction of the total energy of the system. If the energy of the system is small, the fractional change in the total energy of the system will be large when heat is absorbed or released, but if the energy of the system is large, the fractional change in the total energy of the system will be small. That's what  $\beta$  or  $T$  is doing for us. It's adjusting how heat affects the entropy based on the total energy of the system when the heat is absorbed or released.

### Conjugate Pairs, Yet Again

Since  $\beta$  and  $S$  are a conjugate pair<sup>4</sup>,  $T$  and  $S$  are also a conjugate pair (Section 1.5). In this case,  $T$  is the intensive variable (*i.e.*, the generalized force) and  $S$  is the extensive variable (*i.e.*, the generalized displacement). This allows us to write the 1<sup>st</sup> law of thermodynamics as

$$dE = TdS - PdV + \mu dN$$

The parameter  $T$  thus reflects the change in the energy of the system associated with a change in the entropy of the system. This form of the 1<sup>st</sup> law of thermodynamics can also be written as

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

---

<sup>4</sup>See Section 3.5

It follows from this equation that

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N} \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E,N} \quad \frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{V,N} \quad (5.14)$$

### One More Thing

We recall from Equation 4.2 that the dispersion of the energy states of a system is

$$\overline{(\Delta E)^2} = - \frac{\partial \overline{E}}{\partial \beta}$$

As we mentioned earlier, since  $\overline{(\Delta E)^2} \geq 0$ ,  $-\frac{\partial \overline{E}}{\partial \beta} \geq 0$ . We can now express this result in terms of the temperature of the system.

$$\beta = \frac{1}{k_B T} \quad \rightarrow \quad d\beta = - \frac{dT}{k_B T^2}$$

$$\overline{(\Delta E)^2} = - \frac{\partial \overline{E}}{\partial \beta} \quad \rightarrow \quad \overline{(\Delta E)^2} = k_B T^2 \frac{\partial \overline{E}}{\partial T}$$

The dispersion of the energy states of the system increases with increasing temperature. Sure, because increasing the temperature increases the probability (through Boltzmann factors) that higher energy states are populated. This also provides us to revisit the discussion about what  $\beta$  means with respect to an energy reservoir. A high value of  $\beta$  would correspond to a low temperature and a low value of  $\beta$  would correspond to a high temperature. When a system is attached to a low temperature reservoir, only the lowest energy states of the system are populated. In contrast, when a system is attached to a high temperature reservoir, higher energy states of the system are likely to be populated.

## 5.7 Heat Capacity

Combining Equation 1.3 and Equation 5.12 allows us to express the heat capacity in terms of the entropy.

$$C = T \left( \frac{\partial S}{\partial T} \right)$$

Substitution of Equation 5.10 allows us to express the heat capacity in terms of  $\beta$ .

$$C = -\beta \left( \frac{\partial S}{\partial \beta} \right)$$

Thus,

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad C_V = -\beta \left( \frac{\partial S}{\partial \beta} \right)_V \quad (5.15)$$

### Going further

If the only work that can be done by a system is associated with a change in the volume of the system, Equation 5.12 allows us to write the first law of thermodynamics for the system as

$$dE = dQ - dW \quad \rightarrow \quad dE = TdS - PdV$$

Let's now assume that the internal energy is a function of volume and temperature<sup>5</sup>.

$$E = E(V, T) \quad \rightarrow \quad dE = \left( \frac{\partial E}{\partial V} \right)_T dV + \left( \frac{\partial E}{\partial T} \right)_V dT$$

Substitution then gives us

$$\begin{aligned} \left( \frac{\partial E}{\partial V} \right)_T dV + \left( \frac{\partial E}{\partial T} \right)_V dT &= TdS - PdV \\ dS &= \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_V dT + \frac{1}{T} \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] dV \end{aligned}$$

This means that entropy is a function of temperature and volume, as we've seen before, and that we can define the partial derivatives of entropy as

$$\left( \frac{\partial S}{\partial T} \right)_V = \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_V \quad \left( \frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right]$$

And since entropy is an exact differential, the cross partial derivatives must be equal.

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V} \quad \rightarrow \quad \frac{\partial}{\partial V} \left( \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_V \right) = \frac{\partial}{\partial T} \left( \frac{1}{T} \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] \right)$$

$$\frac{1}{T} \frac{\partial^2 E}{\partial V \partial T} = -\frac{1}{T^2} \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] + \frac{1}{T} \left[ \left( \frac{\partial P}{\partial T} \right)_V + \left( \frac{\partial^2 E}{\partial T \partial V} \right)_T \right]$$

And since internal energy is also an exact differential, its cross partial derivatives must be equal

$$\frac{\partial^2 E}{\partial V \partial T} = \frac{\partial^2 E}{\partial T \partial V} \quad \rightarrow \quad 0 = -\frac{1}{T^2} \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] + \frac{1}{T} \left( \frac{\partial P}{\partial T} \right)_V$$

---

<sup>5</sup>We'll ignore the dependence on the number of molecules for now.

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

We're almost there. Now let's go back to the previously derived equation for  $dS$ .

$$dS = \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_V dT + \frac{1}{T} \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] dV$$

We can, of course, write this as

$$TdS = \left( \frac{\partial E}{\partial T} \right)_V dT + \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] dV$$

And when we substitute Equation 1.4 and Equation 5.12 we are left with

$$dQ = C_V dT + \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] dV$$

Substitution into Equation 1.4 then yields

$$C_P = \left( \frac{dQ}{dT} \right)_P \rightarrow C_P = C_V + \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

And since we have just derived that  $P + \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V$ , we have

$$C_P = C_V + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \quad (5.16)$$

It's also worth mentioning that sometimes taking the derivatives in Equation 5.16 is not pleasant. In those cases, it's better to rewrite the expression in terms of related derivatives. For example, we can use our old friend the triple product rule.

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

$$\left( \frac{\partial V}{\partial T} \right)_P = -\frac{1}{\left( \frac{\partial T}{\partial P} \right)_V \left( \frac{\partial P}{\partial V} \right)_T} \rightarrow \left( \frac{\partial V}{\partial T} \right)_P = -\frac{\left( \frac{\partial P}{\partial T} \right)_V}{\left( \frac{\partial P}{\partial V} \right)_T}$$

Therefore,

$$C_P = C_V - T \frac{\left( \frac{\partial P}{\partial T} \right)_V^2}{\left( \frac{\partial P}{\partial V} \right)_T} \quad (5.17)$$



### Heat Capacity For An Ideal Gas

We can calculate  $C_V$  for an ideal gas from the equation for the entropy of the ideal gas using Equation 5.15.

$$C_V = -\beta \left( \frac{\partial}{\partial \beta} \right)_V \left[ k_B N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \right]$$

$$C_V = -\beta \left( -k_B N \frac{3}{2} \frac{1}{\beta} \right) \rightarrow C_V = \frac{3}{2} N k_B$$

We get the same result if we used the other expression for the entropy as all that matters for this calculation is how the entropy of the gas depends on  $\beta$ . This is a common aspect of physics that we've encountered before. Frequently the absolute value of the quantity doesn't matter. What matters is how that quantity changes (*e.g.*, derivatives of the entropy). Probably more important to recognize here, however, is the fact that since heat capacity is proportional to the derivative of the entropy with respect to temperature (or  $\beta$ ), the heat capacity is reporting on the kinetic energy of the gas.

We can calculate  $C_P$  using 5.16

$$C_P = C_V + T \left( \frac{N k_B}{V} \right) \left( \frac{N k_B}{P} \right)$$

$$C_P = C_V + \left( \frac{N k_B T}{P V} \right) N k_B \rightarrow C_P = \frac{5}{2} N k_B$$

As expected,  $C_P > C_V$ , since some of the heat absorbed/released by a system at constant pressure will be devoted to work done by/on the system, leaving less energy to affect the temperature (*i.e.*, to affect the entropy). When the volume is constant, no work can be done, and all the heat absorbed/released affects the temperature.

Alternatively, we could have calculated  $C_P$  directly from the equation for the entropy of the ideal gas. In order to do this, we must first write the equation for the entropy in terms of the pressure of the gas using Equation 5.2.

$$V = \frac{N}{P\beta} \rightarrow S = k_B N \left[ \ln \left( \frac{1}{P\beta} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right]$$

$$C_P = -\beta \left[ k_B N \left( -\frac{1}{\beta} - \frac{3}{2} \frac{1}{\beta} \right) \right] \rightarrow C_P = \frac{5}{2} N k_B$$

As expected, this result is identical to what we derived previously.

#### 5.7.1 A little bit more math

Let's go back to Equation 4.2.

$$\overline{(\Delta E)^2} = -\frac{\partial \overline{E}}{\partial \beta}$$

First, since  $\overline{(\Delta E)^2} \geq 0$  we know that  $-\frac{\partial \bar{E}}{\partial \beta} \geq 0$ . Thus,

$$-\frac{\partial \bar{E}}{\partial \beta} \geq 0 \quad \rightarrow \quad k_B T^2 \frac{\partial \bar{E}}{\partial T} \geq 0$$

In other words, the mean energy of a system must increase as the temperature of the system increases. That's cool and all, but look what happens if we take things a step further

$$\overline{(\Delta E)^2} = k_B T^2 \frac{\partial \bar{E}}{\partial T} \quad \rightarrow \quad \overline{(\Delta E)^2} = k_B T^2 C_V$$

$$C_V = \frac{\overline{(\Delta E)^2}}{k_B T^2}$$

which indicates that the heat capacity is positive. It's also interesting to note that this derivation indicates that the heat capacity must depend on the temperature of the system, both because  $T$  shows up in the equation for  $C_V$  and because  $\overline{(\Delta E)^2}$  is likely temperature dependent.

## 5.8 Chemical Potential

We can calculate the chemical potential for an ideal gas from the equation for the entropy of the ideal gas using Equation 3.26.

$$\mu = -\frac{1}{\beta} \left( \frac{\partial}{\partial N} \right)_{E,V} \left( N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \right)$$

As before, we can substitute  $\beta = \frac{3N}{2E}$  for an ideal gas so that we can take the derivative properly.

$$\mu = -\frac{1}{\beta} \left( \frac{\partial}{\partial N} \right)_{E,V} \left( N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{4Em\pi}{3Nh^2} \right) + \frac{5}{2} \right] \right)$$

$$\mu = -\frac{1}{\beta} \left[ \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] + N \left( -\frac{1}{N} - \frac{3}{2} \frac{1}{N} \right) \right]$$

$$\mu = -\frac{1}{\beta} \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) \right]$$

This expression is usually written in terms of  $\frac{N}{V}$  as that represents the density of the molecules.

$$\mu = \frac{1}{\beta} \left[ \ln \left( \frac{N}{V} \right) - \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) \right] \quad (5.18)$$

When written this way, this expression reflects that lower density corresponds to lower chemical potential. This is consistent with the derivation above about

the approach to diffusive equilibrium. Namely, particles will spontaneously move from high density to low density.

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It's interesting to me that the mean energy, heat capacity, and the pressure of an ideal gas, which do not depend on Planck's constant, can be measured directly

$$\bar{E} = \frac{3}{2}Nk_B T \quad C_V = \frac{3}{2}Nk_B \quad C_P = \frac{5}{2}Nk_B \quad PV = Nk_B T$$

But the entropy and the chemical potential, which do depend on Planck's constant, cannot be measured directly.

$$S = N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \quad \mu = \frac{1}{\beta} \left[ \ln \left( \frac{N}{V} \right) - \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) \right]$$

It makes sense, of course, why this is. Namely, both entropy and chemical potential depend on the volume of the system which means they must depend on how the position phase space is partitioned. This partitioning is the role played by  $h$ .

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## 5.9 Why is Mars red?

What we have derived so far allows us to make a conceptual argument about why Mars is red. We start by normalizing the canonical distribution for a single particle of an ideal gas.

$$1 = \int C e^{-\frac{\beta p^2}{2m}} \frac{dx dy dz 4\pi p^2 dp}{h^3}$$

In effect, we are simply claiming that the particle has to be somewhere in position-momentum phase space. Now let's write this in terms of the speed  $v$ .

$$1 = \int C e^{-\frac{\beta (mv)^2}{2m}} \frac{dx dy dz 4\pi (mv)^2 m dv}{h^3}$$

The integrals over  $dx$ ,  $dy$ , and  $dz$  are simply the volume,  $V$ , of the system.

$$h^3 = 4CV\pi m^3 \int_0^\infty e^{-\frac{\beta m v^2}{2}} v^2 dv \quad \rightarrow \quad h^3 = 4CV\pi m^3 \frac{\sqrt{\frac{\pi}{2}}}{(\beta m)^{\frac{3}{2}}}$$

Thus,

$$C = \frac{h^3}{Vm^3} \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}}$$

It is important to pause here to mention that  $h$  is ignored in most derivations of this speed distribution. So when you use the Google machine to look up this equation, you will very likely not see the  $h^3$  bit. This is fine, as it just means we are dealing with a different constant  $C$  and not a differently shaped distribution. Right? Yes.

If we substitute the value of  $C$  we determined into the normalization equation we have

$$1 = \int \left[ \frac{\cancel{h^3}}{Vm^3} \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} \right] e^{-\frac{\beta mv^2}{2}} \frac{dx \, dy \, dz \, 4\pi(mv)^2 m dv}{\cancel{h^3}}$$

$$1 = \int \left[ \frac{1}{Vm^3} \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} \right] e^{-\frac{\beta mv^2}{2}} dx \, dy \, dz \, 4\pi(mv)^2 m dv$$

Next we cancel out the integral over  $dx$ ,  $dy$ , and  $dz$  with  $V$ .

$$1 = \int \left[ \frac{1}{\cancel{V}m^3} \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} \right] e^{-\frac{\beta mv^2}{2}} \cancel{dx} \, \cancel{dy} \, \cancel{dz} \, 4\pi(mv)^2 m dv$$

$$1 = \int \left[ \frac{1}{m^3} \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} \right] e^{-\frac{\beta mv^2}{2}} 4\pi(mv)^2 m dv$$

And at least some of the  $m$  terms also cancel.

$$1 = \int \left[ \frac{1}{\cancel{m^3}} \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} \right] e^{-\frac{\beta mv^2}{2}} 4\pi(\cancel{m}v)^2 \cancel{m} dv$$

$$1 = \int \left[ \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} \right] e^{-\frac{\beta mv^2}{2}} 4\pi v^2 dv$$

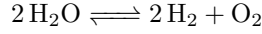
So, it's cool for us to write the probability of finding a gas molecule with speed between  $v$  and  $v + dv$  as

$$P(v)dv = \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} e^{-\frac{\beta mv^2}{2}} 4\pi v^2 dv$$

$$P(v) = 4\pi \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}} e^{-\frac{\beta mv^2}{2}} v^2$$

This expression is named after someone, of course. It's the Maxwell-Boltzmann speed distribution. This is a bit silly, of course, since it's just the canonical distribution.

Now as you may or may not remember from a previous chemistry course, all chemical reactions exist in equilibrium. For example, the dissociation of water into oxygen and hydrogen is described as



We could use the canonical distribution probability we just derived to determine what fraction of the oxygen molecules or hydrogen molecules have a particular speed. These probabilities will be different, of course, since the masses of these molecules of gas are different. So the distribution of speeds for oxygen molecules will be different from the distribution of speeds for hydrogen molecules, and both of these distributions will be a function of temperature (*i.e.*, of  $\beta$ ).

Y'all remember escape speed from classical mechanics? We can solve for it from the equations of for kinetic energy and gravitational potential energy.

$$\frac{1}{2}mv^2 = G\frac{Mm}{R}$$

The variable  $m$  in this equation is the mass of the gas molecule. The variables  $M$  and  $R$  are the mass and radius, respectively, of the planet from which the gas molecule is escaping. Solving for  $v$  gives us

$$v = \sqrt{\frac{2GM}{R}}$$

On Earth, the escape velocity is

$$v = \sqrt{\frac{2 \left( 6.67 \times 10^{-11} \frac{\text{m}^3}{\text{kg s}^2} \right) (5.97 \times 10^{24} \text{kg})}{6.37 \times 10^6 \text{m}}} = 1.12 \times 10^4 \frac{\text{m}}{\text{s}}$$

Assuming an average temperature of 288 K, the probability that a molecule of oxygen or a molecule of hydrogen will have a speed greater than escape speed on Earth is

$$P(\text{H}_2) = 1.7 \times 10^{-22} \quad P(\text{O}_2) = 0$$

Those are pretty small numbers. So, on Earth, when water dissociates into hydrogen and oxygen, both gas molecules hang around within the Earth's atmosphere and can later recombine to form water. Things are different on Mars, though. There, the average temperature is 210 K and the escape velocity is

$$v = \sqrt{\frac{2 \left( 6.67 \times 10^{-11} \frac{\text{m}^3}{\text{s}^2 \text{kg}} \right) (6.39 \times 10^{23} \text{kg})}{3.39 \times 10^6 \text{m}}} = 5.02 \times 10^3 \frac{\text{m}}{\text{s}}$$

Now the probabilities are

$$P(\text{H}_2) = 2.3 \times 10^{-6} \quad P(\text{O}_2) = 0$$

The probability for hydrogen to escape the gravity of Mars is still small, but it's much larger than the probability of hydrogen to escape the gravity of Earth. So, over time, more and more of the hydrogen on Mars will be lost, leaving behind a surplus of oxygen with no hydrogen with which to recombine. Now since oxygen

is a very reactive element, all that extra oxygen will react with other atoms in the atmosphere and soil of Mars, forming things like carbon dioxide and carbon monoxide, as well as interacting with any iron in the soil. It is through this interaction between oxygen and iron that the soil of Mars rusts, turning it red.

## 5.10 Summary

- $\frac{1}{\beta} = k_B T$
- Entropy is also often defined using the Boltzmann constant.

$$S = k_B \ln \Omega$$

- The Second Law of Thermodynamics relates the change in the entropy of a system to the heat absorbed or released by the system by the temperature of the system.

$$dS = \frac{dQ}{T}$$

- Temperature, pressure, and chemical potential of a system can be determined from the equation for the entropy of that system.

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N} \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E,N} \quad \frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{V,N}$$

- The heat capacity of a system can be expressed in terms of the entropy of the system.

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad C_V = -\beta \left( \frac{\partial S}{\partial \beta} \right)_V$$

- $C_P$  and  $C_V$  are related by the relationships between pressure, temperature, and volume.

$$C_P = C_V + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \quad C_P = C_V - T \frac{\left( \frac{\partial P}{\partial T} \right)_V^2}{\left( \frac{\partial P}{\partial V} \right)_T}$$

### Ideal Gas

- $Z = \left[ \left( \frac{eV}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right]^N$
- $\bar{E} = \frac{3N}{2\beta}$
- $S = N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right]$
- $\mu = \frac{1}{\beta} \left[ \ln \left( \frac{N}{V} \right) - \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) \right]$
- $PV = \frac{N}{\beta} \quad PV = Nk_B T$
- $C_V = \frac{3}{2} Nk_B \quad C_P = \frac{5}{2} Nk_B$

**Van der Waals Gas**

- $Z = \left(\frac{Ve}{N}\right)^N \left(\frac{2m\pi}{\beta h^2}\right)^{\frac{3N}{2}} \left[\left(1 - \frac{bN}{V}\right) e^{\beta a \frac{N}{V}}\right]^N$
- $\overline{E} = N \left(\frac{3}{2\beta} - a \frac{N}{V}\right)$
- $\mathcal{S} = N \left[\ln\left(\frac{V-bN}{N}\right) + \frac{3}{2} \ln\left(\frac{2m\pi}{\beta h^2}\right) + \frac{5}{2}\right]$
- $\left(P + a \frac{N^2}{V^2}\right) (V - bN) = \frac{N}{\beta}$