

Chapter 31 Problems: Kinetic Molecular Theory

1. Calculate the average translational kinetic energy in J, cm^{-1} , and kJ mol^{-1} and the rms-speed of CO_2 at 298.2 K, assuming ideal gas behavior.

Answer: The plan is to use Eqs. 31.1.16 and 31.1.18 and note that the rms-speed depends on the molar mass but the average translational kinetic energy does not.

The average translational kinetic energy of any ideal gas at 298.2 K is:

$$\bar{\epsilon}_t = \frac{3}{2} kT = \frac{3}{2} (1.38065 \times 10^{-23} \text{ J K}^{-1})(298.2 \text{ K}) = 6.175 \times 10^{-21} \text{ J}$$

$$\bar{\epsilon}_t = \frac{3}{2} RT = 3.718 \text{ kJ mol}^{-1}$$

$$\bar{\epsilon}_t = 3.718 \text{ kJ mol}^{-1} (1000 \text{ J/1 kJ})(1 \text{ cm}^{-1}/11.9627 \text{ J mol}^{-1}) = 310.8 \text{ cm}^{-1}$$

The values in kJ mol^{-1} and cm^{-1} are useful for comparisons, since we have often noted that the available thermal kinetic energy at room temperature is: $RT = 2.48 \text{ kJ mol}^{-1}$ or 207.2 cm^{-1} .

The molar mass for CO_2 is 44.01 g mol^{-1} or $0.04401 \text{ kg mol}^{-1}$. The rms-speed, using Eq. 31.1.18 is:

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}{0.04401 \text{ kg mol}^{-1}}} = 411.1 \text{ m s}^{-1}$$

To verify the units note that $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$, which is the reason that the molar mass must be in kg mol^{-1} .

2. Calculate the rate of molecular collisions in a balloon filled with N_2 at 298.2 K given the balloon has a 1.00 L volume at 1.00 bar. The hard-core collision diameter is $d_{\text{N}_2} = (2r_{\text{N}_2}) = 3.75 \text{ \AA}$.

Answer: The plan is to use Eq. 31.3.8 to calculate the collision cross section.

The collision cross-section, using Eq. 31.3.8:

$$\sigma_{\text{HC}} = \pi (2r_{\text{N}_2})^2 = \pi [3.75 \times 10^{-10} \text{ m}]^2 = 4.418 \times 10^{-19} \text{ m}^2 = 0.4418 \text{ nm}^2 = 44.18 \text{ \AA}^2$$

The mass of N_2 is: $m = 28.02 \text{ g mol}^{-1} (1 \text{ kg}/1000 \text{ g})/6.0221 \times 10^{23} \text{ mol}^{-1} = 4.653 \times 10^{-26} \text{ kg}$

With Eq. 31.2.31 the average speed of N_2 molecules at 298.2 K is:

$$\bar{c} = \left(\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1})(298.2 \text{ K})}{\pi 4.653 \times 10^{-26} \text{ kg}} \right)^{1/2} = 474.6 \text{ m s}^{-1}$$

The number density is given by the ideal gas law with $1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 1 \times 10^5 \text{ N m}^{-2}$ as:

$$N/V = N_{\text{A}}P/RT = \frac{6.0221 \times 10^{23} \text{ mol}^{-1}(1.00 \times 10^5 \text{ N m}^{-2})}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.2 \text{ K})} = 2.429 \times 10^{25} \text{ m}^{-3}$$

Concerning the units, remember that $1 \text{ J} = 1 \text{ N m}$. Using Eq. 31.3.18 gives the collision rate per cubic meters as:

$$Z_{AA} = \frac{1}{2} \sigma_{HC} \sqrt{2} \bar{c} (N/V)^2 = \frac{1}{2} 4.418 \times 10^{-19} \text{ m}^2 \sqrt{2} (474.6 \text{ m s}^{-1})(2.429 \times 10^{25} \text{ m}^{-3})^2 \\ = 8.75 \times 10^{34} \text{ s}^{-1} \text{ m}^{-3}$$

For the 1.00 L volume:

$$\text{collision rate} = Z_{AA} V = 8.75 \times 10^{34} \text{ s}^{-1} \text{ m}^{-3} (1 \text{ m}^3/1000 \text{ L})(1.00 \text{ L}) = 8.75 \times 10^{31} \text{ s}^{-1}.$$

As mentioned in Example 31.3.1, the total collision rate in a 1 L balloon filled with ambient air is the almost the same.

3. Derive a relationship for the rate of a unimolecular surface-catalyzed reaction of an ideal gas. Assume every collision with the surface gives products and that the rate law is expressed in terms of the gas phase concentration of the reactant in mol L⁻¹.

Answer: The plan is to follow the derivation of the bimolecular rate law, Eqs. 31.3.20-31.3.24 for this specific case.

The rate of collisions per unit area of an ideal gas with a wall is, Eq. 31.3.4:

$$Z_{\text{wall}} = \frac{1}{4} \frac{N}{V} \left(\frac{8RT}{\pi \mathcal{M}} \right)^{1/2} = \frac{1}{4} \frac{N}{V} \bar{c} \quad (31.2.4)$$

for N molecules in total volume V . Given that every collision is successful, for a surface with area A , the rate of the reaction in molecules per second per unit total volume of reactant A is:

$$-\frac{d(N_A/V)}{dt} = Z_{\text{wall}} \frac{A}{V} = \left(\frac{\bar{c}A}{4V} \right) \frac{N_A}{V}$$

The rate is given in molecules per unit volume per unit time. To convert to the rate in mol m⁻³ s⁻¹, we divide the last equation by Avogadro's number:

$$-\frac{d(N_A/N_A V)}{dt} = Z_{\text{wall}} \frac{A}{N_A V} = \left(\frac{\bar{c}A}{4V} \right) \left(\frac{N_A}{N_A V} \right)$$

Using Eq. 31.3.21 for the concentration A:

$$-\frac{d[A]}{dt} = Z_{\text{wall}} \frac{A}{N_A V} = \left(\frac{\bar{c}A}{4V} \right) [A]$$

Expressing the classical rate law as $-d[A]/dt = k_1[A]$ gives the unimolecular rate constant as:

$$k_1 = \left(\frac{\bar{c}A}{4V} \right) = \frac{1}{4} \left(\frac{8RT}{\pi \mathcal{M}} \right)^{1/2} \left(\frac{A}{V} \right)$$

The V in this last equation is in m³ to match the units of $\bar{c}A$. The catalyst surface does not need to be wall-like. This expression, assuming 100% successful collisions, pertains to suspended aerosol particles and liquid droplets as long as the products do not accumulate on the surface and decrease the surface activity.

4. Find the most probable molecular speed using the Maxwell distribution of molecular speeds.

Answer: The plan is to set the derivative of the Maxwell distribution function equal to zero to find the maximum.

The Maxwell distribution of molecular speeds is: $p(c) dc = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2 dc$

Let the normalization constant be $\mathcal{A} = 4\pi (m/2\pi kT)^{3/2}$. Taking the derivative with respect to c using the product rule with the product as $[e^{-mc^2/2kT}][c^2]$ gives:

$$\frac{d p(c)}{dc} = -\mathcal{A} \left(\frac{m}{kT}\right) c e^{-mc^2/2kT} c^2 + 2\mathcal{A} c e^{-mc^2/2kT} = 0$$

Canceling common terms gives: $-\left(\frac{m}{kT}\right) c^2 + 2 = 0$ or $\left(\frac{m}{kT}\right) c^2 = 2$ with $c = c_{mp}$

Solving for c_{mp} gives Eq. 31.2.27: $c_{mp} = \left(\frac{2kT}{m}\right)^{1/2} = \sqrt{\frac{2kT}{m}}$

5. (a). Find the standard deviation of the molecular speed of an ideal gas at temperature T in terms of the molar mass. (b). Find the most probable, average, and rms-speeds and standard deviation of the speed of CO_2 at 298.2 K.

Answer: The plan is to note that $\sigma^2 = \overline{(c - \bar{c})^2} = \overline{c^2} - (\bar{c})^2$, Eq. 23.4.36. See also Problem 1.

(a). First, in case you haven't done it before, we derive $\sigma^2 = \overline{(c - \bar{c})^2} = \overline{c^2} - (\bar{c})^2$. Starting with the squared deviation from the mean:

$$(c - \bar{c})^2 = c^2 - 2c\bar{c} + (\bar{c})^2$$

Next we need to take the average. Because the average speed is a constant, the average of a constant is just that constant:

$$\overline{(c)} = \bar{c} \quad \text{and} \quad \overline{(\bar{c})^2} = (\bar{c})^2$$

Taking the averages of each term: $\sigma^2 = \overline{(c - \bar{c})^2} = \overline{c^2} - 2\bar{c}\bar{c} + (\bar{c})^2 = \overline{c^2} - (\bar{c})^2$

Now from Eqs. 31.1.18 and 31.2.31 and $8/\pi = 2.546$:

$$\sigma^2 = \overline{c^2} - (\bar{c})^2 = \frac{3RT}{\mathcal{N}} - \frac{8RT}{\pi\mathcal{N}} = 0.4535 \frac{RT}{\mathcal{N}} \quad \text{or} \quad \sigma = \sqrt{\frac{0.4535 RT}{\mathcal{N}}} = 0.673 \sqrt{\frac{RT}{\mathcal{N}}}$$

(b). The molar mass for CO_2 is 44.01 g mol⁻¹ or 0.04401 kg mol⁻¹.

The most probable speed, using Eq. 31.2.27 is:

$$c_{mp} = \sqrt{\frac{2 RT}{\mathcal{N}}} = \sqrt{\frac{2 (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}{0.04401 \text{ kg mol}^{-1}}} = 335.6 \text{ m s}^{-1}$$

The average speed, using Eq. 32.2.31 is:

$$\bar{c} = \sqrt{\frac{8 RT}{\pi \mathcal{M}}} = \sqrt{\frac{8 (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}{\pi 0.04401 \text{ kg mol}^{-1}}} = 378.7 \text{ m s}^{-1}$$

The rms-speed, using Eq. 32.1.18 is:

$$u = \sqrt{\frac{3 RT}{\mathcal{M}}} = \sqrt{\frac{3 (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}{0.04401 \text{ kg mol}^{-1}}} = 411.1 \text{ m s}^{-1}$$

The standard deviation is : $\sigma = \sqrt{\frac{0.4535 RT}{\mathcal{M}}} = 0.673 \sqrt{\frac{RT}{\mathcal{M}}} = 159.7 \text{ m s}^{-1}$

In conventional notation we can state: $\bar{c} = 378.7 \pm 159.7 \text{ m s}^{-1}$, which is a considerable spread in velocities.

Note that for a symmetrical, purely-Gaussian distribution, the rms-speed is equal to the standard deviation. For the Maxwell distribution of molecular speeds the final distribution is unsymmetrical with a long tail at high velocity.

6. (a). Show that the rms-speed is given by the pressure P and mass density d by : $u = \sqrt{3P/d}$.
 (b). At 1.01325 bar and 373.2 K the density of water vapor is 598 g m^{-3} . Calculate the rms-speed of water molecules in water vapor.

Answer: The plan is to note that the mass and number density are related by $d = N\mathcal{M}/(N_A V)$.

First we need to verify that $d = N\mathcal{M}/(N_A V)$, which we can do by checking the units:

$$d = N\mathcal{M}/(N_A V) \sim (\text{molecules})(\text{g mol}^{-1})/[(\text{molecules mol}^{-1})(\text{m}^3)] = \text{g m}^{-3}$$

Then solving for the number density gives: $N/V = N_A d/\mathcal{M}$. The pressure is given by Eq. 31.1.14:

$$P = \frac{N m u^2}{3V} \tag{31.1.14}$$

Substituting in $N/V = N_A d/\mathcal{M}$ for the number density gives: $P = \frac{m u^2 N_A d}{3 \mathcal{M}} = \frac{u^2 d}{3}$

noting that $N_A m = \mathcal{M}$. Then solving for the rms-speed gives: $u = \sqrt{3P/d}$

(b). For unit agreement the pressure is $P = 1.01325 \times 10^5 \text{ Pa} = 1.01235 \times 10^5 \text{ N m}^{-2}$ and the density is $d = 0.598 \text{ kg m}^{-3}$, giving:

$$u = \sqrt{3P/d} = \sqrt{3(1.01325 \times 10^5 \text{ N m}^{-2})/(0.598 \text{ kg m}^{-3})} = 713 \text{ m s}^{-1}$$

With $\mathcal{M} = 18.02 \text{ g mol}^{-1} = 0.01802 \text{ kg mol}^{-1}$ and using Eq. 31.1.18, the value is:

$$u = \sqrt{\frac{3 RT}{\mathcal{M}}} = \sqrt{\frac{3 (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(373.2 \text{ K})}{0.01802 \text{ kg mol}^{-1}}} = 718.7 \text{ m s}^{-1}$$

The difference is caused by experimental error in the gas phase density and non-ideality.

7. A compound with molar mass of 255.2 g mol^{-1} is placed in a small container that has a hole of radius 0.0500 mm . In 30.0 min at 50.0°C , 0.872 g of the substance effuses from the container. Calculate the vapor pressure of the substance.

Answer: The plan is to use the effusion rate from Eq. 31.3.6.

$$\text{The effusion rate is: } \frac{dn}{dt} = \frac{0.872 \text{ g}}{(255.2 \text{ g mol}^{-1})(30.0 \text{ min})(60 \text{ s/1 min})} = 1.898 \times 10^{-6} \text{ mol s}^{-1}$$

The hole area is $A = \pi(0.050 \times 10^{-3} \text{ m})^2 = 7.854 \times 10^{-9} \text{ m}^2$. The molar mass is $0.2552 \text{ kg mol}^{-1}$.

$$\text{The effusion rate, Eq. 31.3.6, is: } \frac{dn}{dt} = PA \left(\frac{1}{2\pi nRT} \right)^{1/2}$$

$$\begin{aligned} \text{Solving for the pressure gives: } P &= \frac{(2\pi nRT)^{1/2}}{A} \frac{dn}{dt} \\ &= \frac{[2\pi(0.2552 \text{ kg mol}^{-1})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(323.2 \text{ K})]^{1/2}}{7.854 \times 10^{-9} \text{ m}^2} (1.898 \times 10^{-6} \text{ mol s}^{-1}) \\ &= 1.586 \times 10^4 \text{ N m}^{-2} = 0.1586 \text{ bar} = 15.86 \text{ kPa} \end{aligned}$$

In alternate units: $P = 0.1586 \text{ bar} (1 \text{ atm}/1.01325 \text{ bar}) = 0.1566 \text{ atm} = 119. \text{ torr}$

8. A compound with a vapor pressure of 1.680 kPa is placed in a small container closed by a metal membrane with a 0.0500 mm radius hole. The initial mass is 123.5 mg . After 30.0 min at 35.0°C the mass decreases to 39.9 mg . Calculate the molar mass of the substance.

Answer: The plan is to convert the effusion rate in Eq. 31.3.6 to the rate in kg s^{-1} by multiplying by the molar mass.

The effusion rate in kg s^{-1} is obtained by multiplying Eq. 31.3.6 by the molar mass in kg mol^{-1} :

$$r = \frac{d(nM)}{dt} = PA M \left(\frac{1}{2\pi nRT} \right)^{1/2} = PA M^{1/2} \left(\frac{1}{2\pi RT} \right)^{1/2} \quad 1$$

Solving this expression for the molar mass in kg mol^{-1} gives: $M = \frac{2\pi RT}{P^2 A^2} r^2 \quad 2$

$$\text{The effusion rate is: } r = \frac{d(nM)}{dt} = \frac{0.0836 \text{ g}(1 \text{ kg}/1000 \text{ g})}{(30.0 \text{ min})(60 \text{ s}/1 \text{ min})} = 4.644 \times 10^{-8} \text{ kg s}^{-1} \quad 3$$

The area of the hole is $A = \pi(0.050 \times 10^{-3} \text{ m})^2 = 7.854 \times 10^{-9} \text{ m}^2$.

With Eq. 2 the molar mass is:

$$M = \frac{2\pi RT}{P^2 A^2} r^2 = \frac{2\pi(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(308.2 \text{ K})}{(1.680 \times 10^3 \text{ N m}^{-2})^2 (7.854 \times 10^{-9} \text{ m}^2)^2} (4.644 \times 10^{-8} \text{ kg s}^{-1}) = 0.1994 \text{ kg mol}^{-1}$$

or $M = 199.4 \text{ g mol}^{-1}$. Concerning the units, $1 \text{ N} = 1 \text{ J m}^{-1} = 1 \text{ kg m s}^{-2}$ and $1 \text{ N m}^{-2} = 1 \text{ J m}^{-3}$.

$$\frac{2\pi RT}{P^2 A^2} r^2 \sim \frac{J K^{-1} \text{mol}^{-1} (K)}{(J m^{-3})^2 (m^2)^2} (kg s^{-1})^2 \sim \frac{\text{mol}^{-1}}{J m^{-2}} (kg^2 s^{-2}) \sim \frac{\text{mol}^{-1}}{(kg m^2 s^{-2}) m^{-2}} (kg^2 s^{-2}) \sim kg \text{ mol}^{-1}$$

9. Integrals of the form $\int_0^{x_c} e^{-ax^2} dx$ are common in determining the probability of occurrence of speeds or energies within a given range. The integral has no closed form solution and must be integrated numerically. The numerical integrals in dimensionless form are tabulated as the error function, $\text{erf}()$, where the error function is defined by:

$$\frac{2}{\sqrt{\pi}} \int_0^t e^{-y^2} dy = \text{erf}(t)$$

The error function is used extensively in statistics and probability. The inside back cover lists a short table. Extensive tables are available in standard reference sources and Excel has an $\text{erf}()$ function. In this regard $\text{erf}()$ is similar to the more familiar functions $\sin()$, $\cos()$, $\exp()$ and $\ln()$, which are all evaluated as power series expansions.

(a). Show that: $\int_0^{x_c} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2} \text{erf}(\sqrt{a} x_c)$

(b). Verify the result in part (a) by showing that $\int_0^{\infty} e^{-ax^2} dx$ gives the result listed in standard integral tables.

(c). Show the probability of a molecule having a velocity in the x-direction in the range $\pm v^*$ is:

$$\int_{-v^*}^{v^*} p(v_x) dv_x = 2 \int_0^{v^*} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x = \text{erf}\left(\sqrt{mv^{*2}/2kT}\right)$$

(d). Show that the probability of a molecule having a kinetic energy in the x-direction less than or equal to kT is 84.3%. [Hint: note that $\text{erf}(1) = 0.8427$]

Answer: For part (a) the plan is to do a change of variables. For part (c) the plan is to use the integral in part (a) with $a = m/2kT$. The plan for part (d) is to note that $\epsilon_t = \frac{1}{2} mv^2$

(a). Comparing the definition of the error function to $\int_0^{x_c} e^{-ax^2} dx$ requires the change of variables $y^2 = ax^2$ or equivalently $y = \sqrt{a} x$ with derivative and corresponding differential:

$$\frac{dy}{dx} = \sqrt{a} \quad \text{with } dx = \frac{1}{\sqrt{a}} dy \quad \text{and upper limit } t = \sqrt{a} x_c$$

then substituting for ax^2 and dx gives:

$$\int_0^{x_c} e^{-ax^2} dx = \frac{1}{\sqrt{a}} \int_0^t e^{-y^2} dy = \frac{1}{\sqrt{a}} \frac{\sqrt{\pi}}{2} \text{erf}(t) = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2} \text{erf}(\sqrt{a} x_c)$$

(b). Tables of $\text{erf}(t)$ show that the function approaches one for large values of t . In other words, $(2/\sqrt{\pi}) \int_0^t e^{-y^2} dy$ is normalized. Setting $x_c = \infty$ gives $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} (\pi/a)^{1/2}$ as listed in standard definite integral tables.

(c). The distribution function is even so that $\int_{-v^*}^{v^*} = 2 \int_0^{v^*}$. For the one-dimensional velocity distribution with $a = m/2kT$ and $x_c = v^*$ using the integral in part (a) gives:

$$\int_{-v^*}^{v^*} p(v_x) dv_x = 2 \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^{v^*} e^{-mv_x^2/2kT} dv_x = \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{2\pi kT}{m} \right)^{1/2} \operatorname{erf}(\sqrt{mv^{*2}/2kT})$$

$$= \operatorname{erf}(\sqrt{mv^{*2}/2kT})$$

(d). Note that $\varepsilon_t = kT$ gives $\frac{1}{2} mv^{*2} = kT$ and $mv^{*2}/2kT = 1$ with $\operatorname{erf}(1) = 0.8427$.

Note that $\operatorname{erf}(1) = 0.8427$ is the area under a Gaussian distribution within $x = \pm\sqrt{2} \sigma$.

10. Derive the integration by parts formula using the following steps: (a). Let u and v be two functions. Using the product rule for the differential $d(uv)$, show that $\int d(uv) = \int v du + \int u dv$. (b). Finally show that for the integral limits u_1v_1 to u_2v_2 :

$$\int u dv = uv \Big|_{u_1v_1}^{u_2v_2} - \int v du$$

Answer: (a). Using the product rule $d(uv) = vdu + u dv$. Integrating both sides of the equation gives: $\int d(uv) = \int v du + \int u dv$.

(b). Solving for $\int u dv$ gives: $\int u dv = \int d(uv) - \int v du$

The integral of $\int d(uv)$ is just uv evaluated at the limits of the integral: $\int_{u_1v_1}^{u_2v_2} d(uv) = uv \Big|_{u_1v_1}^{u_2v_2}$.

Substituting this result for the integral gives the final result: $\int u dv = uv \Big|_{u_1v_1}^{u_2v_2} - \int v du$.

11. Integrals over the Maxwell distribution of molecular speeds are in the general form

$\int_0^t y^2 e^{-y^2} dy$. Use integration by parts, $\int u dv = uv \Big|_{u_1v_1}^{u_2v_2} - \int v du$, with $u = y$ and $dv = (y e^{-y^2} dy)$ to show that: [See the next problem for an application of this relationship.]

$$\frac{4}{\sqrt{\pi}} \int_0^t y^2 e^{-y^2} dy = \operatorname{erf}(t) - \frac{2}{\sqrt{\pi}} t e^{-t^2}$$

Answer: The plan is to start by integrating dv to give v in terms of y .

With $u = y$ and $dv = (y e^{-y^2} dy)$ then: $du = dy$ and $v = \int dv = \int y e^{-y^2} dy = -\frac{1}{2} e^{-y^2}$

Integration by parts gives: $\int u dv = uv \Big|_{u_1v_1}^{u_2v_2} - \int v du$

$$\int_0^t y^2 e^{-y^2} dy = -\frac{1}{2} y e^{-y^2} \Big|_0^t - (-\frac{1}{2}) \int_0^t e^{-y^2} dy$$

The integral is given by the error function: $(2/\sqrt{\pi}) \int_0^t e^{-y^2} dy = \operatorname{erf}(t)$. The first term is evaluated at the limits and substituting in the error function gives:

$$\int_0^t y^2 e^{-y^2} dy = -\frac{1}{2} t e^{-t^2} + \frac{\sqrt{\pi}}{4} \operatorname{erf}(t)$$

The required integral is then: $\frac{4}{\sqrt{\pi}} \int_0^t y^2 e^{-y^2} dy = \operatorname{erf}(t) - \frac{2}{\sqrt{\pi}} t e^{-t^2}$

See the next problem for an application of this relationship.

12. The probability of occurrence of molecular speeds over a range of values is determined by an integral over the distribution function. (a). Show that the integral of the Maxwell distribution of molecular speeds over the range from $c = 0$ to c^* is:

$$\int_0^{c^*} p(c) dc = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{c^*} e^{-mc^2/2kT} c^2 dc = \operatorname{erf}(\sqrt{mc^{*2}/2kT}) - \frac{1}{\sqrt{\pi}} \sqrt{\frac{mc^{*2}}{2kT}} e^{-mc^{*2}/2kT}$$

(b). The kinetic energy at the upper limit is $\varepsilon_t^* = \frac{1}{2}mc^{*2}$. Show that the total probability is:

$$\int_0^{c^*} p(c) dc = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{c^*} e^{-mc^2/2kT} c^2 dc = \operatorname{erf}(\sqrt{\varepsilon_t^*/kT}) - \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon_t^*}{kT} \right)^{1/2} e^{-\varepsilon_t^*/kT}$$

[Hint: use the relationship in the previous problem with the change in variables $y^2 = mc^2/2kT$]

Answer: (a). With the substitution $y^2 = mc^2/2kT$ then $y = (m/2kT)^{1/2} c$ and the derivative is:

$$\frac{dy}{dc} = (m/2kT)^{1/2} \quad \text{giving} \quad dc = \left(\frac{2kT}{m} \right)^{1/2} dy \quad \text{with} \quad c^2 = \left(\frac{2kT}{m} \right) y^2$$

and upper limit $t = (m/2kT)^{1/2} c^*$. The integral over the Maxwell distribution is:

$$\begin{aligned} \int_0^{c^*} p(c) dc &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{c^*} e^{-mc^2/2kT} c^2 dc = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\frac{2kT}{m} \right) \left(\frac{2kT}{m} \right)^{1/2} \int_0^t y^2 e^{-y^2} dy \\ &= \frac{4}{\sqrt{\pi}} \int_0^t y^2 e^{-y^2} dy \end{aligned}$$

Using the relationship derived in the previous problem gives:

$$\int_0^{c^*} p(c) dc = \operatorname{erf}(t) - \frac{2}{\sqrt{\pi}} t e^{-t^2}$$

The substitution variable is conveniently regrouped as $y = (m/2kT)^{1/2} c = (mc^2/2kT)^{1/2}$

Reversing the original substitution then gives:

$$\int_0^{c^*} p(c) dc = \operatorname{erf}(\sqrt{mc^{*2}/2kT}) - \frac{2}{\sqrt{\pi}} \sqrt{\frac{mc^{*2}}{2kT}} e^{-mc^{*2}/2kT}$$

Or given that the kinetic energy at the upper limit of the speed is $\varepsilon_t^* = \frac{1}{2}mc^{*2}$:

$$\int_0^{c^*} p(c) dc = \operatorname{erf}(\sqrt{\varepsilon_t^*/kT}) - \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon_t^*}{kT} \right)^{1/2} e^{-\varepsilon_t^*/kT}$$

13. Determine the probability that a molecule has a speed equal to or less than the most probable speed. [Hint: Use the relationship in the previous problem, note that $\operatorname{erf}(1) = 0.8427$]

Answer: The plan is to note that the most probable speed is given by Eq. 31.2.27.

The upper limit on the integral is $c^* = c_{mp}$. With Eq. 31.2.27 the most probable speed is:

$$c_{\text{mp}} = \left(\frac{2kT}{m}\right)^{1/2} = \sqrt{\frac{2kT}{m}}$$

The corresponding translational kinetic energy is: $\varepsilon_t^* = \frac{1}{2} m c_{\text{mp}}^2 = kT$.

As a result the factor appearing in the result is: $\sqrt{\varepsilon_t^*/kT} = 1$

The probability that a molecule has a speed equal to or less than the most probable speed is then:¹

$$\begin{aligned} \int_0^{c^*} p(c) dc &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{c^*} e^{-mc^2/2kT} c^2 dc = \text{erf}(1) - \frac{2}{\sqrt{\pi}} 1^{1/2} e^{-1} \\ &= 0.8427 - \frac{2}{\sqrt{\pi}} 0.3679 = 0.8427 - 0.4151 = 0.4276 \quad \text{or} \quad 42.8\% \end{aligned}$$

The fraction above the most probable speed is $1 - 0.4276 = 0.572$ or 57.2%

14. The fraction of molecules with translational kinetic energy exceeding ε^* is:^{1,2}

$$p(\varepsilon_t > \varepsilon^*) = \int_{\varepsilon^*}^{\infty} p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_{\varepsilon^*}^{\infty} \varepsilon_t^{1/2} e^{-\varepsilon_t/kT} d\varepsilon_t$$

(a). Use the change of variable $x^2 = \varepsilon_t/kT$ to show: [Hint: see Eq. 31.4.5 for a similar change in variables.]

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2 e^{-x^2} dx$$

(b). Use integration by parts to show: [Hint: let $u = x$ and $dv = x e^{-x^2} dx$]

$$\int_{x^*}^{\infty} x^2 e^{-x^2} dx = -\frac{1}{2} x e^{-x^2} \Big|_{x^*}^{\infty} - (-\frac{1}{2}) \int_{x^*}^{\infty} e^{-x^2} dx$$

(c). Show that: $\int_{x^*}^{\infty} e^{-x^2} dx = \int_0^{\infty} e^{-x^2} dx - \int_0^{x^*} e^{-x^2} dx$

(d). Use integral tables and the definition of the error function: $\frac{2}{\pi^{1/2}} \int_0^t e^{-x^2} dx = \text{erf}(t)$ to show that:

$$\int_{x^*}^{\infty} e^{-x^2} dx = \frac{\sqrt{\pi}}{2} - \frac{\sqrt{\pi}}{2} \text{erf}(x^*)$$

(e). Using the previous expressions, derive the final result:

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2 e^{-x^2} dx = \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{1/2} e^{-\varepsilon^*/kT} + 1 - \text{erf}\left(\left[\frac{\varepsilon^*}{kT}\right]^{1/2}\right)$$

(f). Show that for large threshold energies, $\varepsilon^* \gg kT$: $p(\varepsilon_t > \varepsilon^*) \cong \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{1/2} e^{-\varepsilon^*/kT}$

Answer: (a). We can simplify the integral with the change in variables $x^2 = \varepsilon_t/kT$ or $\varepsilon_t = kTx^2$:

$$\frac{d\varepsilon_t}{dx} = kT \frac{dx^2}{dx} = 2kTx \quad \text{giving} \quad d\varepsilon_t = 2kTx dx \quad \text{and} \quad \varepsilon_t^{1/2} = (kT)^{1/2} x \quad 1$$

with the limits from $x^* = (\varepsilon^*/kT)^{1/2}$ to ∞ :

$$p(\varepsilon_t > \varepsilon^*) = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} (2kT)(kT)^{1/2} \int_{x^*}^{\infty} x^2 e^{-x^2} dx$$

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2 e^{-x^2} dx \quad 2$$

(b). There is no closed-form solution to the integral, so we need to relate the integrals to the error function. To integrate by parts, let $u = x$ and $dv = x e^{-x^2} dx$ giving:

$$du = dx \quad \text{and} \quad v = \int dv = \int x e^{-x^2} dx = -\frac{1}{2} e^{-x^2} \quad 3$$

so that: $\int u dv = uv \Big|_{u_1 v_1}^{u_2 v_2} - \int v du$ is:

$$\int_{x^*}^{\infty} x^2 e^{-x^2} dx = -\frac{1}{2} x e^{-x^2} \Big|_{x^*}^{\infty} - (-\frac{1}{2}) \int_{x^*}^{\infty} e^{-x^2} dx \quad 4$$

(c). The first term evaluated at the limits is $\frac{1}{2} x^* e^{-x^{*2}}$. For the second integral note that:

$$\int_0^{\infty} e^{-x^2} dx = \int_0^{x^*} e^{-x^2} dx + \int_{x^*}^{\infty} e^{-x^2} dx \quad 5$$

which gives the integral we want by difference:

$$\int_{x^*}^{\infty} e^{-x^2} dx = \int_0^{\infty} e^{-x^2} dx - \int_0^{x^*} e^{-x^2} dx \quad 6$$

(d). Standard integral tables give $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2}$, giving: $\int_0^{\infty} e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$ 7

The $\int_0^{x^*} e^{-x^2} dx$ integral is given by the error function: $\frac{2}{\pi^{1/2}} \int_0^t e^{-x^2} dx = \text{erf}(t)$ with $t = x^*$ or:

$$\text{As a result: } \int_0^{x^*} e^{-x^2} dx = \frac{\sqrt{\pi}}{2} \text{erf}(x^*) \quad 8$$

Substituting Eqs. 7 and 8 into Eq. 6 gives:

$$\int_{x^*}^{\infty} e^{-x^2} dx = \frac{\sqrt{\pi}}{2} - \frac{\sqrt{\pi}}{2} \text{erf}(x^*) \quad 9$$

(e). Substituting the last equation into Eq. 4 gives:

$$\int_{x^*}^{\infty} x^2 e^{-x^2} dx = \frac{1}{2} x^* e^{-x^{*2}} + \frac{\sqrt{\pi}}{4} - \frac{\sqrt{\pi}}{4} \text{erf}(x^*) \quad 10$$

Substituting this last result into Eq. 2 with $x^2 = \varepsilon_t/kT$ gives:

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2 e^{-x^2} dx = \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{1/2} e^{-\varepsilon^*/kT} + 1 - \text{erf}\left(\left(\frac{\varepsilon^*}{kT}\right)^{1/2}\right) \quad 11$$

(f). As ε^* increases, the error function approaches 1, so that for large threshold energies.

$$p(\varepsilon_t > \varepsilon^*) \cong \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{1/2} e^{-\varepsilon^*/kT} \quad (32.4.9)$$

The $(\varepsilon^*/kT)^{1/2}$ temperature dependence is weaker than the exponential term so that the fraction of translational-energy rich molecules increases roughly as $e^{-\varepsilon^*/kT}$ with increases in temperature.

15. Find the most probable translational kinetic energy of an ideal gas using the Maxwell distribution of translational kinetic energy.

Answer: The plan is to set the derivative of the Maxwell distribution of translational kinetic energy equal to zero to find the maximum.

The Maxwell distribution of translational kinetic energy, Eq. 31.4.3, is:

$$p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\varepsilon_t/kT} \varepsilon_t^{1/2} d\varepsilon_t$$

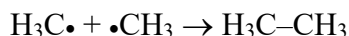
Let the normalization constant be $\mathcal{A} = 2\pi (1/\pi kT)^{3/2}$. Taking the derivative with respect to ε_t using the product rule with the product as $[e^{-\varepsilon_t/kT}][\varepsilon_t^{1/2}]$ gives:

$$\frac{d p(\varepsilon_t)}{d\varepsilon_t} = -\mathcal{A} \left(\frac{1}{kT}\right) e^{-\varepsilon_t/kT} \varepsilon_t^{1/2} + \frac{1}{2}\mathcal{A} \varepsilon_t^{-1/2} e^{-\varepsilon_t/kT} = 0$$

Canceling common terms gives: $-\left(\frac{1}{kT}\right) \varepsilon_t^{1/2} + \frac{1}{2} \varepsilon_t^{-1/2} = 0$ or $\left(\frac{1}{kT}\right) \varepsilon_t = \frac{1}{2}$ with $\varepsilon_t = \varepsilon_{mp}$

Solving for ε_{mp} gives: $\varepsilon_{mp} = \frac{1}{2} kT$

16. The rate constant for the recombination of methyl radicals is $4.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ at 398.2 K.



The reaction has no activation energy. Assuming the hard-core collision radii of the methyl radicals are one-half the normal C–C bond length, $r_{\text{CH}_3} = 0.77 \text{ \AA}$, calculate the bimolecular rate constant assuming hard-core collision theory at 398.2 K.³

Answer: The plan is to follow Example 31.3.2.

The collision cross-section, using Eq. 31.3.8, is:

$$\sigma_{\text{HC}} = \pi (2r_{\text{CH}_3})^2 = \pi [2(0.77 \times 10^{-10} \text{ m})]^2 = 7.45 \times 10^{-20} \text{ m}^2 = 0.0745 \text{ nm}^2 = 7.45 \text{ \AA}^2$$

The molar mass of $\cdot\text{CH}_3$ is 15.03 g mol^{-1} . The reduced mass of the collision is:

$$\mu = \left(\frac{\mathcal{M}_A \mathcal{M}_B}{\mathcal{M}_A + \mathcal{M}_B}\right) \frac{1}{N_A} (1 \text{ kg}/1000 \text{ g}) = \frac{15.03 \text{ g mol}^{-1}}{2} \frac{1}{N_A} (1 \text{ kg}/1000 \text{ g}) = 1.248 \times 10^{-26} \text{ kg}$$

With Eq. 31.3.14 the relative speed is:

$$\bar{c}_{\text{rel}} = \left(\frac{8(1.3806 \times 10^{-23} \text{ J K}^{-1})(398.2 \text{ K})}{\pi 1.248 \times 10^{-26} \text{ kg}}\right)^{1/2} = 1059.1 \text{ m s}^{-1}$$

Assuming each collision is successful, the rate constant is predicted to be, Eq. 31.3.25:

$$k_2 = \sigma_{\text{HC}} \bar{c}_{\text{rel}} (1000 \text{ L/m}^3) N_A = 7.45 \times 10^{-20} \text{ m}^2 (1059.1 \text{ m s}^{-1})(1000 \text{ L/m}^3) 6.022 \times 10^{23} \text{ mol}^{-1} \\ = 4.75 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$$

This result suggests that roughly each collision is successful (or that the estimate of the collision cross section is too small). The rough agreement of the experimental rate constant and the hard-core prediction indicates that the steric requirements of the reaction are minimal; the orientation of the methyl radicals upon collision is largely immaterial.

17. (a). Show that the density of states of a one-dimensional particle in a box is:

$$\rho(\epsilon_x) d\epsilon_x = (8m)^{1/2} \frac{a}{h} (\epsilon_x)^{-1/2} d\epsilon_x$$

[Hint: you don't need to use the graphical approach that we used for three-dimensions.]

(b). Compare the behavior of the one-dimensional and three-dimensional particle in a box as a function of energy. Why the difference with the change in dimensionality?

Answer: The plan is to determine the derivative of the energy with respect to the quantum number n_x ; the final relationship should be written in terms of the energy (and not the quantum number).

$$(a). \text{ The one-dimensional particle in a box energy, Eq. 23.4.9, is: } \epsilon_x = \frac{h^2}{8ma^2} n_x^2 \quad 1$$

$$\text{The density of states is given by the derivative, Eq. 31.6.5: } \rho(\epsilon_x) d\epsilon_x = \frac{dn_x}{d\epsilon_x} d\epsilon_x \quad 2$$

$$\text{The derivative is much easier as the inverse: } \frac{dn_x}{d\epsilon_x} = \left(\frac{d\epsilon_x}{dn_x}\right)^{-1} \text{ with } \frac{d\epsilon_x}{dn_x} = \frac{h^2}{8ma^2} (2 n_x) \quad 3$$

However, we need to eliminate the dependence on the quantum number. Solving Eq. 1 for the quantum number gives: $n_x = (8m\epsilon_x)^{1/2} \frac{a}{h}$ 4

$$\text{Substituting Eq. 4 into Eq. 3 gives: } \frac{d\epsilon_x}{dn_x} = \frac{h^2}{8ma^2} (8m\epsilon_x)^{1/2} \frac{a}{h} = \frac{\epsilon_x^{1/2}}{(8m)^{1/2}} \frac{h}{a} \quad 5$$

Inverting this last equation gives the density of states as: $\rho(\epsilon_x) d\epsilon_x = (8m)^{1/2} \frac{a}{h} (\epsilon_x)^{-1/2} d\epsilon_x$

(b). The density of states decreases as $(\epsilon_x)^{-1/2}$ with increasing energy, as shown in Figures 23.4.2 and 23.4.4. The density of states of the three-dimensional particle in a box increases with energy as $\epsilon_x^{1/2}$. The difference is the result of degeneracy. The one-dimensional problem is not degenerate but Figure 31.6.1 shows the 3D-problem to be highly degenerate, which increases the density of states.

18. Calculate the number of translational energy states at 298.2 K for O_2 in a box of volume 1.00 m^3 with energies from kT to $1.001 kT$ (i.e. a 0.1% change in energy).

Answer: The plan is to use the density of states in three-dimensions, Eq. 31.6.8.

The mass of O₂ is $m = \mathcal{M}/N_A$ (1 kg/1000 g) = 5.314×10^{-26} kg. Using Eq. 31.6.8 with $\varepsilon_t = kT$:

$$\begin{aligned}\varepsilon_t = kT &= 4.116 \times 10^{-21} \text{ J} \\ \rho(kT) &= \frac{\pi}{4} (8m)^{3/2} \frac{V}{h^3} (kT)^{1/2} \\ &= \frac{\pi}{4} [8(5.314 \times 10^{-26} \text{ kg})]^{3/2} \frac{1 \text{ m}^3}{(6.6261 \times 10^{-34} \text{ J s})^3} [(1.3806 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})]^{1/2} \\ &= 4.801 \times 10^{52} \text{ J}^{-1}\end{aligned}$$

With the energy range as $\delta\varepsilon_t = 0.001 kT = 4.116 \times 10^{-24}$ J giving the number of states as:

$$\rho(\varepsilon_t) \delta\varepsilon_t = 4.801 \times 10^{52} (4.116 \times 10^{-24} \text{ J}) = 1.98 \times 10^{29}$$

In other words, lots of available states. Concerning the units: $1 \text{ J s} = \text{kg m}^2 \text{ s}^{-1}$ and then:

$$\rho(\varepsilon_t) = \frac{\pi}{4} (8m)^{3/2} \frac{V}{h^3} \varepsilon_t^{1/2} \sim \text{kg}^{3/2} \frac{\text{m}^3}{(\text{kg m}^2 \text{ s}^{-1})^3} (\text{kg m}^2 \text{ s}^{-2})^{1/2} \sim \frac{1}{\text{kg m}^2 \text{ s}^{-2}} \sim \text{J}^{-1}$$

19. (a). For a square box with side length a and area $A = a^2$, show that the density of states of a two-dimensional particle in a box is:

$$\rho(\varepsilon_t) d\varepsilon_t = 2\pi m \frac{A}{h^2} d\varepsilon_t$$

The two-dimensional case has some applicability to free translational motion on a surface and electrical conduction in restricted geometries. (b). The density of states of a one-dimensional particle in a box is given in the previous problem. Compare the one, two, and three-dimensional cases in terms of the behavior with respect to increasing energy. (c). Find the two-dimensional Maxwell distribution of translational kinetic energy.

Answer: The plan is to note that this derivation is similar to Eqs. 31.6.4-31.6.8, with graphical areas instead of volumes.

(a). The quantum numbers of the two-dimensional particle in a box are combined as $n^2 = n_x^2 + n_y^2$.

$$\text{The energy is: } \varepsilon_t = \frac{h^2}{8ma^2} (n_x^2 + n_y^2) = \frac{h^2}{8ma^2} n^2 \quad 1$$

The density of states is required, Eq. 31.6.5:

$$\rho(\varepsilon_t) = \frac{dN(\varepsilon_t)}{d\varepsilon_t} \quad 2$$

The number of quantum states up to energy ε_t can be determined using a graphical analogy. Each choice of quantum numbers, n_x , n_y is represented as a point in an x-y coordinate plot. Each unit change of n_x , and n_y corresponds to a unit area square. Each unit of area corresponds to one specific value of n_x , and n_y . The maximum value of n for states with energy less than or equal to ε_t is calculated by solving Eq. 1 for n :

$$n_{\max} = (8m)^{1/2} \left(\frac{a}{h}\right) \varepsilon_t^{1/2} \quad (31.6.6) \quad 3$$

The total number of states with energies between zero and ε_t is given by $1/4$ of the area of the circle with radius n_{\max} . The factor of $1/4$ is necessary because a circle centered on the origin is divided into quarters, but only one-quarter has both positive x and y values. The area of a circle is πr^2 , which gives the number of states with energy from zero to ε_t as:

$$N(\varepsilon_t) = \frac{1}{4} \pi n_{\max}^2 = \left(\frac{\pi}{4}\right) (8m) \left(\frac{a}{h}\right)^2 \varepsilon_t = 2\pi m \frac{A}{h^2} \varepsilon_t \quad 4$$

The density of states is the derivative with respect to ε_t , Eq. 31.6.5:

$$\rho(\varepsilon_t) = \frac{dN(\varepsilon_t)}{d\varepsilon_t} = 2\pi m \frac{A}{h^2} \quad \text{or finally} \quad \rho(\varepsilon_t) d\varepsilon_t = 2\pi m \frac{A}{h^2} d\varepsilon_t \quad 5$$

(b). The density of states is constant with increasing kinetic energy. For one-dimension the density decreases as $(\varepsilon_x)^{-1/2}$, for two-dimensions the density is constant as $(\varepsilon_t)^0$, and for three-dimensions the density increases as $\varepsilon_t^{1/2}$. The density of states of a one-dimensional system decreases because the non-degenerate energy states of a one-dimensional box diverge with increasing quantum number. The density of states of a three-dimensional system increases because of the large degeneracy of high energy translational levels.

(c). Given the area A , the two dimensional distribution function, in analogy with Eq. 32.6.3, is:

$$p(\varepsilon_t) dn = \frac{n_i}{N} = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT) A/h^2} dn \quad n^2 = n_x^2 + n_y^2 \quad 6$$

Substituting the density of states into Eq. 6 to complete the change in variables from dn to $d\varepsilon_t$ gives:

$$p(\varepsilon_t) d\varepsilon_t = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT) A/h^2} \rho(\varepsilon_t) d\varepsilon_t = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT) A/h^2} 2\pi m \frac{A}{h^2} d\varepsilon_t \quad 7$$

Canceling common terms gives the two-dimensional Maxwell distribution of translational kinetic energy:

$$p(\varepsilon_t) d\varepsilon_t = \left(\frac{1}{kT}\right) e^{-\varepsilon_t/kT} d\varepsilon_t \quad 8$$

As a check, if we did things correctly, the final result should automatically be normalized:

$$\int_0^\infty p(\varepsilon_t) d\varepsilon_t = \left(\frac{1}{kT}\right) \int_0^\infty e^{-\varepsilon_t/kT} d\varepsilon_t \quad 9$$

Integral tables list $\int_0^\infty e^{-ax} dx = 1/a$ and since $a = 1/kT$, the integral is equal to one.

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