

## Week 3

# Kinetic Theory of Gases / The First Law of Thermodynamics

### 3.1 Maxwell-Boltzmann Distribution

- 1/24:
- Applying the molecular partition function to the heat capacity of a water molecule.
    - A water molecule has three vibrational modes, which we will denote by  $\nu_1, \nu_2, \nu_3$  (corresponding to symmetric stretch, antisymmetric stretch, and bend).
    - Main takeaway: Heat capacity can change with temperature.
    - After a while (at several thousand kelvin), it will level off (see Figure 18.7).
  - Considers CO<sub>2</sub>'s vibrational modes, too.
    - The infrared absorption of the bending mode is what's associated with the Greenhouse Effect.
    - The symmetric stretch is IR inactive due to its lack of change of dipole moment.
    - Raman active: Change in the polarizability of the molecule.
  - The Maxwell-Boltzmann distribution.
    - Maxwell derived it long before Boltzmann, but Boltzmann's thermodynamic derivation is much easier.
    - We know from the Boltzmann factor that  $p(E) \propto e^{-E/k_B T}$ .
    - Thus, to get the probability  $p(v)$  of some speed  $v$ , we should have  $p(v) \propto e^{-mv^2/2k_B T}$  times a constant giving the number of molecules of each speed? This yields

$$p(v) = A4\pi v^2 e^{-mv^2/2k_B T}$$

where  $A$  is a normalization constant.

- The Maxwell-Boltzmann distribution is such that

$$\begin{aligned} 1 &= \int_0^\infty p(v) \, dv \\ &= A \int_0^\infty 4\pi v^2 e^{-mv^2/2k_B T} \, dv \\ &= A \int_0^\infty 4\pi \left( \frac{2k_B T}{m} \right)^{3/2} u^2 e^{-u^2} \, du \\ &= A4\pi \left( \frac{2k_B T}{m} \right)^{3/2} \int_0^\infty u^2 e^{-u^2} \, du \end{aligned}$$

$$= A4\pi \left( \frac{2k_B T}{m} \right)^{3/2} \frac{\sqrt{\pi}}{4}$$

$$A = \left( \frac{m}{2\pi k_B T} \right)^{3/2}$$

– Therefore,

$$p(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

– Any distribution that doesn't look like this isn't in thermal equilibrium.

- A system with all particles having  $v = 0$  is at thermal equilibrium with  $T = 0$  K.
- A system with all particles having constant velocity in the same direction is at thermal equilibrium with  $T = 0$  K.
  - Think relativity; if you're moving with them, it looks like they're not moving and thus this case is the same as the last one because your movement doesn't affect the thermodynamics of that system.
- A system with all particles having constant velocity in different directions is not at thermal equilibrium since it does not fit the bell curve but is rather a spike.

### 3.2 The First Law of Thermodynamics

1/26:

- See Labalme (2021b) for background on/content of today's lecture.
- Joule best quantified how we think about work and energy.
- **System:** Part of the world being investigated. It can contain energy, a number of particles, etc.
- The Newtonian way to change the energy into a system is to do work (mechanical, electrical, etc.) on the system. In chemistry,  $\delta w$  is positive if work is done on the system.
  - We have that

$$\delta w = -P dV$$

- A system at thermal equilibrium has a given temperature characteristic of the system. Some property of the system indicates how hot or cold it is (e.g., volume of mercury, etc.)
- Measure heat transfer using a calorimeter and a thermometer.
  - Convention: Heat put into a system  $\delta q$  is positive and this heat is transferred if the temperature is lower than another system or surroundings.
  - The heat capacity of a system times the change in temperature is equal to the heat put into the system. It is always positive as heat put into the system raises the temperature.
- Example molar heat capacities.
  - For water vapor at low pressure and 20 °C,  $\overline{C}_V = 3R = 25 \text{ J mol}^{-1} \text{ K}^{-1}$ .
  - For liquid water, it's higher (hydrogen bonding).
  - For ice, it's lower.
- **First law of thermodynamics:** The internal energy of a system changes with heat put into the system and work done on the system.

$$dU = \delta q + \delta w$$

– Note that in engineering,  $dU = \delta q - \delta w$ .

- **State variable:** A property that describes the system.
  - For example, a system of gas molecules has a state defined by the state variables  $T$ ,  $P$ ,  $V$ , and  $n$ .
- **State function:** A property that depends only upon the state of the system.
  - For example, some equations of state for an ideal gas are  $PV = nRT$  or  $PV = 2U/3$ .
  - The internal energy is a state function.
  - Heat and work are not state functions because they do not depend uniquely on the values at equilibrium.
    - They also depend on the way you do something.
- **Reversible process:** A process that can be represented as a path along state variables, e.g., a line on a  $PV$  diagram. This implies that it is also a path where all state variables are known, and is therefore a path where the system is always in quasi-equilibrium.
  - Isothermal, isochoric, isobaric, and adiabatic changes are reversible.
  - All of these processes are analyzed exactly as in Labalme (2021b).
- **Irreversible process:** A process that cannot be drawn on a  $PV$  diagram.
- Experiment to measure  $\gamma$  (the ratio of specific heats):
  1. Let sit at  $P_0 T_0$ .
  2. Pump in a little gas (add  $\Delta n$ ) and let sit, measure  $P_0 + \Delta P_1, T_0$ .
  3. Open the valve to air quickly to  $P_0$ . Adiabatic expansion (cools down).
  4. Let sit to measure the new pressure  $P + \Delta P_2$  when  $T$  is back at  $T_0$ .
  5.  $\gamma$  is determined from  $\Delta P_1, \Delta P_2$  (this will be a homework problem).
  - In the second step, we add some molecules into the container. We can show that  $\Delta P_1/P_0 = \Delta N_1/n_0$ .
  - In the third step, we let out the air, and we can show that  $\Delta n_2/n_0 = \gamma \Delta P_1/P_0$ .
  - In step 4, we have in the container  $(n_0 + \Delta n_1 - \Delta n_2)RT_0 = (P_0 + \Delta P_2)V_0$ .
  - This implies that  $\Delta P_2/\Delta P_1 = 1 - 1/\gamma$ .

### 3.3 Enthalpy

- 1/28:
- Thermodynamic derivation of the formula for  $\langle P \rangle$  in terms of  $Q$ .
    - We have that

$$\begin{aligned}
 U &= \sum p_j E_j \\
 dU &= \sum (dp_j E_j + p_j dE_j) \\
 &= \underbrace{\sum dp_j E_j}_{\delta q} + \underbrace{\sum p_j \frac{\partial E_j}{\partial V} dV}_{-P}
 \end{aligned}$$

where the last part follows by analogy with  $dU = \delta q - P dV$ .

- It follows that

$$P = - \sum p_j \frac{\partial E_j}{\partial V} = - \left\langle \frac{\partial E}{\partial V} \right\rangle$$

- Thus, we have that

$$\begin{aligned}
 P &= - \sum \frac{e^{-E_j/k_B T}}{Q} \frac{\partial E_j}{\partial V} \\
 &= \frac{1}{Q} \sum k_B T \cdot - \frac{1}{k_B T} e^{-E_j/k_B T} \frac{\partial E_j}{\partial V} \\
 &= k_B T \frac{1}{Q} \sum \frac{\partial}{\partial E_j} \left( e^{-E_j/k_B T} \right) \frac{\partial E_j}{\partial V} \\
 &= k_B T \frac{1}{Q} \sum \frac{\partial}{\partial V} \left( e^{-E_j/k_B T} \right) \\
 &= k_B T \frac{1}{Q} \frac{\partial Q}{\partial V} \\
 P &= k_B T \frac{\partial \ln Q}{\partial V}
 \end{aligned}$$

- Applies the formula to an ideal gas of independent, indistinguishable particles to derive the ideal gas law.
- **Enthalpy:** A state function representign the heat put into the system at constant pressure. *Denoted by  $H$ . Given by*

$$H = U + PV$$

- We have that

$$\begin{aligned}
 dH &= dU + P dV + V dP \\
 &= \delta q - P dV + P dV + V dP \\
 &= \delta q + V dP
 \end{aligned}$$

- At constant pressure ( $dP = 0$ ), we have that  $dH = \delta q$ .
- At constant volume, we have that  $dH = \delta q$  as well?

- **Constant-volume heat capacity.** The following expression. *Denoted by  $C_V$ . Given by*

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N}$$

- **Constant-pressure heat capacity.** The following expression. *Denoted by  $C_P$ . Given by*

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P,N}$$

- For an ideal gas,

$$\begin{aligned}
 dH &= dU + d(PV) \\
 &= nC_V dT + nR dT \\
 &= n(C_V + R) dT
 \end{aligned}$$

- Recall this result from Labalme (2021b).

- Considers heat diagrams.

- Recall the enthalpy of phase changes  $\Delta H_{\text{fus}}$ ,  $\Delta H_{\text{vap}}$ , and  $\Delta H_{\text{sub}}$ .
- It follows that

$$H(T) - H(T_0) = \int_{T_0}^T C_p dT + \sum \Delta H_{\text{phase changes}}$$

- **Hess's Law:**  $\Delta H = 0$  around a closed loop.
  - This is because  $H$  is a state function.
- **Standard enthalpy of formation.** The enthalpy of formation of a substance, as calculated from its constituent elements in their standard state (i.e., 1 bar, 298.15 K). Denoted by  $\Delta H_f^\circ$ . Units **kJ/mol**.
- We have, for example, that the  $\Delta H_{\text{vap}}^\circ$  of a substance is the difference of its  $\Delta H_f^\circ$  in its gaseous state and its  $\Delta H_f^\circ$  in its liquid state.
- With the standard enthalpy of formation and the heat capacity  $C_P(T)$ , one gets the enthalpy of formation at nonstandard temperatures.
- To get the enthalpy of formation at non-standard pressures of chemical interest, most of the effect is from the gas components because solids and liquid enthalpy vary little with pressure.
- The direction of change is sometimes in the direction of *positive* enthalpy change.
  - This change is driven by the fact that in these cases, the direction of change is toward the most probable state.
- In a reversible process,  $dU = \delta q_{\text{rev}} - P dV$ . In this case

$$\delta q_{\text{rev}} = dU + P dV = nC_V dT + P dV \neq d(nC_V T + PV)$$

so  $\delta q_{\text{rev}}$  is not a state function.

- However,

$$\begin{aligned} \frac{\delta q_{\text{rev}}}{T} &= nC_V \frac{dT}{T} + \frac{P dV}{T} \\ &= nC_V \frac{dT}{T} + nR \frac{dV}{V} \\ &= d(nC_V \ln T + nR \ln V) \end{aligned}$$

is a state function.

### 3.4 Chapter 27: The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

1/30:

- **Kinetic theory of gases:** A simple model of gases in which the molecules (pictured as hard spheres) are assumed to be in constant, incessant motion, colliding with each other and with the walls of the container.
- McQuarrie and Simon (1997) does the KMT derivation of the ideal gas law from Labalme (2021a). Some important notes follow.
  - McQuarrie and Simon (1997) emphasizes the importance of

$$PV = \frac{1}{3}Nm \langle u^2 \rangle$$

as a fundamental equation of KMT, as it relates a macroscopic property  $PV$  to a microscopic property  $m \langle u^2 \rangle$ .

- In Chapter 17-18, we derived quantum mechanically, and then from the partition function, that the average translational energy  $\langle E_{\text{trans}} \rangle$  for a single particle of an ideal gas is  $\frac{3}{2}k_B T$ . From classical mechanics, we also have that  $\langle E_{\text{trans}} \rangle = \frac{1}{2}m \langle u^2 \rangle$ . *This* is why we may let

$$\frac{1}{2}m \langle u^2 \rangle = \frac{3}{2}k_B T$$

recovering that the average translational kinetic energy of the molecules in a gas is directly proportional to the Kelvin temperature.

- **Isotropic** (entity): An object or substance that has the same properties in any direction.
  - For example, a homogeneous gas is isotropic, and this is what allows us to state that  $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$ .
- McQuarrie and Simon (1997) derives

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

- $u_{\text{rms}}$  is an estimate of the average speed since  $\langle u^2 \rangle \neq \langle u \rangle^2$  in general.
- McQuarrie and Simon (1997) states without proof that the speed of sound  $u_{\text{sound}}$  in a monatomic ideal gas is given by

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

- Assumptions of the kinetic theory of gases.
  - Particles collide elastically with the wall.
    - Justified because although each collision will not be elastic (the particles in the wall are moving too), the average collision will be elastic.
  - Particles do not collide with each other.
    - Justified because “if the gas is in equilibrium, on the average, any collision that deflects the path of a molecule... will be balanced by a collision that replaces the molecule” (McQuarrie & Simon, 1997, p. 1015).
- Note that we can do the kinetic derivation at many levels of rigor, but more rigorous derivations offer results that differ only by constant factors on the order of unity.
- Deriving a theoretical equation for the distribution of the *components* of molecular velocities.
  - Let  $h(u_x, u_y, u_z) du_x du_y du_z$  be the fraction of molecules with velocity components between  $u_j$  and  $u_j + du_j$  for  $j = x, y, z$ .
  - Assume that the each component of the velocity of a molecule is independent of the values of the other two components<sup>1</sup>. It follows statistically that

$$h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

- Note that we use just one function  $f$  for the probability distribution in each direction because the gas is isotropic.
- We can use the isotropic condition to an even greater degree. Indeed, it implies that any information conveyed by  $u_x$  is necessarily and sufficiently conveyed by  $u_y$ ,  $u_z$ , and  $u$ . Thus, we may take

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

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<sup>1</sup>This can be proven.

- It follows that

$$\frac{\partial \ln h(u)}{\partial u_x} = \frac{\partial}{\partial u_x} (\ln f(u_x) + \text{terms not involving } u_x) = \frac{d \ln f(u_x)}{du_x}$$

- Since

$$\begin{aligned} u^2 &= u_x^2 + u_y^2 + u_z^2 \\ \frac{\partial}{\partial u_x} (u^2) &= \frac{\partial}{\partial u_x} (u_x^2 + u_y^2 + u_z^2) \\ 2u \frac{\partial u}{\partial u_x} &= 2u_x \\ \frac{\partial u}{\partial u_x} &= \frac{u_x}{u} \end{aligned}$$

we have that

$$\begin{aligned} \frac{\partial \ln h}{\partial u_x} &= \frac{d \ln h}{du} \frac{\partial u}{\partial u_x} = \frac{u_x}{u} \frac{d \ln h}{du} \\ \frac{d \ln h(u)}{u du} &= \frac{d \ln f(u_x)}{u_x du_x} \end{aligned}$$

which generalizes to

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x} = \frac{d \ln f(u_y)}{u_y du_y} = \frac{d \ln f(u_z)}{u_z du_z}$$

- Since  $u_x, u_y, u_z$  are independent, we know that the above equation is equal to a constant, which we may call  $-\gamma$ . It follows that for any  $j = x, y, z$ , we have that

$$\begin{aligned} \frac{d \ln f(u_j)}{u_j du_j} &= -\gamma \\ \frac{1}{f} \frac{df}{du_j} &= -\gamma u_j \\ \int \frac{df}{f} &= \int -\gamma u_j du_j \\ \ln f &= -\frac{\gamma}{2} u_j^2 + C \\ f(u_j) &= A e^{-\gamma u_j^2} \end{aligned}$$

where we have incorporated the  $1/2$  into  $\gamma$ .

- To determine  $A$  and  $\gamma$ , we let arbitrarily let  $j = x$ . Since  $f$  is a continuous probability distribution, we may apply the normalization requirement.

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} f(u_x) du_x \\ &= 2A \int_0^{\infty} e^{-\gamma u_x^2} du_x \\ &= 2A \sqrt{\frac{\pi}{4\gamma}} \\ A &= \sqrt{\frac{\gamma}{\pi}} \end{aligned}$$

- Additionally, since we have that  $\langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$  and  $\langle u^2 \rangle = 3RT/M$ , we know that  $\langle u_x^2 \rangle = RT/M$ . This combined with the definition of  $\langle u_x^2 \rangle$  as a continuous probability distribution yields

$$\begin{aligned} \frac{RT}{M} &= \langle u_x^2 \rangle \\ &= \int_{-\infty}^{\infty} u_x^2 f(u_x) \, du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} u_x^2 e^{-\gamma u_x^2} \, du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}} \\ &= \frac{1}{2\gamma} \\ \gamma &= \frac{M}{2RT} \end{aligned}$$

- Therefore,

$$f(u_x) = \sqrt{\frac{M}{2\pi RT}} e^{-Mu_x^2/2RT}$$

- It is common to rewrite the above in terms of molecular quantities  $m$  and  $k_B$ .
- It follows that as temperature increases, more molecules are likely to be found with higher component velocity values.
- We can use the above result to show that

$$\langle u_x \rangle = \int_{-\infty}^{\infty} u_x f(u_x) \, du_x = 0$$

- We can also calculate that  $\langle u_x^2 \rangle = RT/M$  and  $m \langle u_x \rangle^2 / 2 = k_B T / 2$  from the above result<sup>[2]</sup>.
  - An important consequence is that the total kinetic energy is divided equally into the  $x$ -,  $y$ -, and  $z$ -components. This fact was also demonstrated in Week 1, Lecture 3.
- **Doppler broadening:** The broadening of spectral lines due to the distribution of molecular velocities.
  - Ideally, spectral lines will be very narrow.
  - However, due to the Doppler effect, if an atom or molecule emits radiation of frequency  $\nu_0$  while moving away or toward the observer with speed  $u_x$ , then the observed frequency will be

$$\nu \approx \nu_0 \left( 1 + \frac{u_x}{c} \right)$$

- Indeed, “if one observes the radiation emitted from a gas at temperature  $T$ , then it is found that the spectral line at  $\nu_0$  will be spread out by the Maxwell distribution of  $u_x$  of the molecule emitting the radiation” (McQuarrie & Simon, 1997, p. 1021).
- It follows by the definition of  $f(u_x)$  and the above that

$$I(\nu) \propto e^{-mc^2(\nu-\nu_0)^2/2\nu_0^2 k_B T}$$

i.e., that  $I(\nu)$  is of the form of a Gaussian centered at  $\nu_0$  with variance  $\sigma^2 = \nu_0^2 k_B T / mc^2$ .

- **Deriving Maxwell-Boltzmann distribution.**

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<sup>2</sup>See the equipartition of energy theorem from Labalme (2021b).



- Let the probability that a molecule has speed between  $u$  and  $u + du$  be defined by a continuous probability distribution  $F(u) du$ . In particular, we have from the above isotropic condition that

$$\begin{aligned} F(u) du &= f(u_x) du_x f(u_y) du_y f(u_z) du_z \\ &= \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-m(u_x^2 + u_y^2 + u_z^2)/2k_B T} du_x du_y du_z \end{aligned}$$

- Considering  $F$  over a **velocity space**, we realize that we may express the probability distribution  $F$  as a function of  $u$  via  $u^2 = u_x^2 + u_y^2 + u_z^2$  and the differential volume element in every direction over the sphere of equal velocities (a sphere by the isotropic condition) by  $4\pi u^2 du = du_x du_y du_z$ .
- Thus, the Maxwell-Boltzmann distribution in terms of speed is

$$F(u) du = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu^2/2k_B T} du$$

- **Maxwell-Boltzmann distribution:** The distribution of molecular speeds.

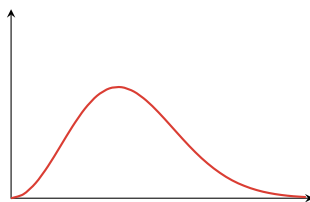


Figure 3.1: The Maxwell-Boltzmann distribution.

- **Velocity space:** A rectangular coordinate system in which the distances along the axes are  $u_x, u_y, u_z$ .
- We may use the above result to calculate that

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi m}}$$

which only differs from  $u_{\text{rms}}$  by a factor of 0.92.

- **Most probable speed:** The most probable speed of a gas molecule in a sample that obeys the Maxwell-Boltzmann distribution. Denoted by  $u_{\text{mp}}$ . Given by

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

- Derived by setting  $dF/du = 0$ .

- We may also express the Maxwell-Boltzmann distribution in terms of energy via  $u = \sqrt{2\varepsilon/m}$  and  $du = d\varepsilon / \sqrt{2m\varepsilon}$  to give

$$F(\varepsilon) d\varepsilon = \frac{2\pi}{(\pi k_B T)^{3/2}} \sqrt{\varepsilon} e^{-\varepsilon/k_B T} d\varepsilon$$

- We can also confirm our previously calculated values for  $\langle u^2 \rangle$  and  $\langle \varepsilon \rangle$ .
- McQuarrie and Simon (1997) does a higher-level derivation of the ideal gas law that is rather analogous to the one done in class (i.e., via its flux perspective).
- McQuarrie and Simon (1997) discusses a simple and Nobel-prize winning experiment that verified the Maxwell-Boltzmann distribution.

### 3.5 Chapter 19: The First Law of Thermodynamics

From McQuarrie and Simon (1997).

- 1/31:
- **Thermodynamics:** The study of various properties and, particularly, the relations between the various properties of systems in equilibrium.
    - Primarily an experimental science that is still of great practical value to the fields of today.
    - “All the results of thermodynamics are based on three fundamental laws. These laws summarize an enormous body of experimental data, and there are absolutely no known exceptions” (McQuarrie & Simon, 1997, p. 765).
  - **Classical thermodynamics:** The development of thermodynamics before the atomic theory of matter.
    - Since thermodynamics was not developed in concert with the atomic theory, we can rest assured that its results will not need to be modified. However, it provides limited insight into what is going on at the molecular level.
  - **Statistical thermodynamics:** The molecular interpretation of thermodynamics developed since the atomic theory of matter became generally accepted.
    - Chapters 17-18 are an elementary treatment of statistical thermodynamics.
    - Since atomic structure is still being determined, these results are not on as solid of a footing as classical thermodynamics.
  - **First Law of Thermodynamics:** The law of conservation of energy applied to a macroscopic system.
  - **System:** The part of the world we are investigating.
  - **Surroundings:** Everything else.
  - **Heat:** The manner of energy transfer that results from a temperature difference between the system and its surroundings. *Denoted by  $q$ .*
    - Sign convention: Heat input into a system is positive; heat evolved by a system is negative.
  - **Work:** The transfer of energy between the system of interest and its surroundings as a result of the existence of unbalanced forces between the two. *Denoted by  $w$ .*
    - Sign convention: Work done *on* the system (i.e., that increases the energy of the system) is positive; work done *by* the system (i.e., that increases the energy of the surroundings) is negative.
  - Work can be related to raising a mass.
    - If a pressurized gas is capped by a piston with a mass  $m$  on top and then it pushes the piston upwards a distance  $h$ , it does  $w = -mgh$  of work.
    - Knowing that the external pressure  $P_{\text{ext}} = F/A = mg/A$  and  $Ah = \Delta V$ , we recover

$$w = -P_{\text{ext}}\Delta V$$

- If  $P_{\text{ext}}$  is not constant,

$$w = - \int_{V_i}^{V_f} P_{\text{ext}} dV$$

- **Definite state:** A state of a system in which all of the variables needed to describe the system completely are defined.

- For example, the state of one mole of an ideal gas can be described completely via  $P$ ,  $V$ , and  $T$ . In fact, we need only specify two of these since  $PV = RT$  for one mole of gas (in particular, specifying any two specifies the third).
- **State function:** A property that depends only upon the state of the system, not upon how the system was brought to that state.
  - State functions can be integrated in a normal way, i.e.,  $\Delta U = U_2 - U_1 = \int_1^2 dU$ . In particular, we need not worry about the *path* from state 1 to state 2, only that we got from  $U_1$  to  $U_2$ .
  - Energy is a state function, but work and heat are not state functions.
- **Reversible process:** An expansion or compression in which  $P_{\text{ext}}$  and  $P$  differ only infinitesimally.
  - Technically, a reversible process would take infinite time, but it serves as a useful idealized limit regardless.
- To calculate  $w_{\text{rev}}$  (reversible work) for the compression of an ideal gas isothermally, we may replace  $P_{\text{ext}}$  by the pressure of the gas  $P$  to obtain

$$w_{\text{rev}} = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

- Isothermal compression/expansion of a gas.

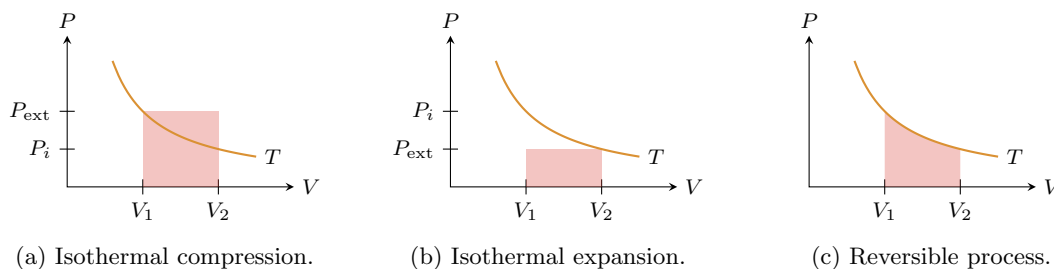


Figure 3.2: Isothermal manipulation of an ideal gas.

- Imagine a gas at pressure  $P$ , volume  $V$ , and temperature  $T$  in a container with a moveable piston at the top.
- Isothermal compression (Figure 3.2a).
  - Let the external pressure be held constant at  $P_{\text{ext}}$ . If the volume of the gas is initially at  $V_2$  and temperature  $T$ , its pressure will be  $P_i$ . Thus, to equilibrate with the external pressure, it will compress to volume  $V_1$  and final pressure  $P_f = P_{\text{ext}}$  along the isotherm. As the force doing this work is the constant external pressure, the work done will be encapsulated by the red box in Figure 3.2a. Note that the gas necessarily releases an amount of heat equivalent to the work in the red box during the course of the compression to maintain isothermal conditions.
- Isothermal expansion (Figure 3.2a).
  - Let the external pressure be held constant at  $P_{\text{ext}}$ . If the volume of the gas is initially at  $V_1$  and temperature  $T$ , its pressure will be  $P_i$ . Thus, to equilibrate with the external pressure, it will expand to volume  $V_2$  and final pressure  $P_f = P_{\text{ext}}$  along the isotherm. As the force doing this work is the constant external pressure, the work done will be encapsulated by the red box in Figure 3.2a. Note that the gas necessarily absorbs an amount of heat equivalent to the work in the red box during the course of the expansion to maintain isothermal conditions.
- Reversible compression/expansion (Figure 3.2c).

- In a very slow manner, incrementally increase (resp. decrease)  $P_{\text{ext}}$  so as to allow the gas to reversibly compress (resp. expand).
- Compressing a gas reversibly and isothermally does the minimum amount of work on the gas. Expanding a gas reversibly and isothermally requires the gas to do the maximum amount of work.
- This work done on the gas raises the internal energy of the system, right? So shouldn't that raise the temperature, making the process not isothermal?
- Where does the extra energy above and below the isotherm in the irreversible processes go? Is it converted to heat?
- Does this mean that if you used a 1000 kg weight to compress a gas to half its original volume vs. using a 10 kg weight to compress a gas to half its original volume, the gas would get 100 times hotter in the former case?
- **Path function:** A function whose value depends on the path from state 1 to state 2, not just the initial and final states.
  - Path functions cannot be integrated in the normal way. Mathematically, they have **inexact differentials**, i.e., we write  $\int_1^2 \delta w = w$ . This is because it makes no sense to write  $w_1$ ,  $w_2$ ,  $w_2 - w_1$ , or  $\Delta w$ , for example.
  - Work and heat are path functions.
- The First Law of Thermodynamics says that  $dU = \delta q + \delta w$  (in differential form) and  $\Delta U = q + w$  (in integrated form).
  - An important consequence is that even though  $\delta q$  and  $\delta w$  are separately path functions/inexact differentials, their sum is a state function/exact differential.
- **Adiabatic process:** A process in which no heat is transferred between the system and its surroundings.
- Work during an adiabatic process.
  - For an adiabatic process,  $\delta q = 0$ .
  - Thus,  $w = \Delta U$ .
  - But since  $\Delta U$  is entirely dependent on temperature, we have that

$$w = \Delta U = \int_{T_1}^{T_2} \left( \frac{\partial U}{\partial T} \right)_V dT = \int_{T_1}^{T_2} C_V(T) dT$$

- Why isn't this an integral of  $P$  with respect to  $V$ ?

- Temperature during an adiabatic process.
  - We have that

$$\begin{aligned} dU &= dw \\ C_V(T) dT &= -P dV \\ n\bar{C}_V(T) dT &= -\frac{nRT}{V} dV \\ \int_{T_1}^{T_2} \frac{\bar{C}_V(T)}{T} dT &= -R \int_{V_1}^{V_2} \frac{dV}{V} \end{aligned}$$

- In the specific case of a monatomic ideal gas,  $C_V(T) = 3/2$ . Thus, continuing, we have

$$\begin{aligned} \frac{3}{2} \ln \frac{T_2}{T_1} &= \ln \frac{V_1}{V_2} \\ \left( \frac{T_2}{T_1} \right)^{3/2} &= \frac{V_1}{V_2} \end{aligned}$$

- We can also express the above in terms of pressure

$$\left(\frac{P_2 V_2 / nR}{P_1 V_2 / nR}\right)^{3/2} = \frac{V_1}{V_2}$$

$$P_1 V_1^{5/3} = P_2 V_2^{5/3}$$

- For a diatomic gas, we end up with

$$P_1 V_1^{7/5} = P_2 V_2^{7/5}$$

- Note that for an isothermal expansion, Boyle's law applies:  $P_1 V_1 = P_2 V_2$ .

- Relating work and heat to molecular properties.

- By comparing recently derived equations with previously derived equations, we have that

$$U = \sum_j p_j E_j$$

$$dU = \sum_j p_j dE_j + \sum_j E_j dp_j$$

$$= \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV + \sum_j E_j dp_j$$

- The above equation suggests that we can interpret the first term as the average change in energy of a system caused by a small change in its volume, i.e., the average work.
- It follows by the First Law of Thermodynamics that we can interpret the second term as the average heat.
- This expresses the important but subtle notion that work results from “an infinitesimal change in the allowed energies of a system, without changing the probability distribution of its states” while heat results from “a change in the probability distribution of the states of a system, without changing the allowed energies” (McQuarrie & Simon, 1997, p. 780).
- In particular, if we take the process under study to be reversible, we have

$$dU = \underbrace{\sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV}_{\delta w_{\text{rev}}} + \underbrace{\sum_j E_j dp_j}_{\delta q_{\text{rev}}} = \underbrace{\sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV}_{-P} + \sum_j E_j dp_j$$

- The second equality above expresses the fact that

$$P = -\left\langle \frac{\partial E}{\partial V} \right\rangle$$

which we previously used in Chapter 17.

- For a constant-volume process,  $w = 0$ , so we know that the heat evolved in the process  $q_V = \Delta U$ .
- Defining a state function analogous to  $U$  for constant-pressure processes.

- We have from the First Law that

$$\Delta U = q + w = q - \int_{V_1}^{V_2} P dV$$

- Thus, at constant pressure,

$$q_P = \Delta U + P_{\text{ext}} \int_{V_1}^{V_2} dV = \Delta U + P \Delta V$$

– The above equation suggests how to define our new state function.

- **Enthalpy:** The state function describing the heat put into a system at constant pressure. *Denoted by  $H$ . Given by*

$$H = U + PV$$

–  $\Delta H$  can be determined experimentally as the heat associated with a constant-pressure process.

- Examples.

– For the melting of ice,  $\Delta V$  is small, so  $\Delta U \approx \Delta H$ .

– For the vaporization of water,  $\Delta V$  is large, so  $\Delta U < \Delta H$ .

- We interpret the excess by the fact that most of the energy goes into raising the internal energy of the water (i.e., breaking the hydrogen bonding), but some of it must go into increasing the volume of the system against the atmospheric pressure.

- For reactions or processes that involve ideal gases,

$$\Delta H = \Delta U + RT\Delta n_{\text{gas}}$$

where  $\Delta n_{\text{gas}}$  is the difference in the number of moles of gaseous products vs. reactants.

- **Extensive quantity:** A quantity that depends on the amount of substance.

– Heat capacity is an extensive quantity.

- Heat capacity is a path function, as it depends on whether we heat the substance at constant volume or constant pressure.

- We have

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \qquad C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

– We expect  $C_P > C_V$  since we also have to work against atmospheric pressure.

– In fact, for a monatomic ideal gas,

$$\begin{aligned} H &= U + PV \\ &= U + nRT \\ \frac{dH}{dT} &= \frac{dU}{dT} + nR \\ C_P - C_V &= nR \\ C_P &= \frac{3}{2}R + nR \\ &= \frac{5}{2}R \end{aligned}$$

– It follows that the difference between  $C_P$  and  $C_V$  is significant for gases, but not for solids and liquids.

– Note that we can also prove a general expression for  $C_P - C_V$  (see Chapter 22).

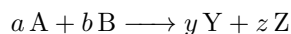
- Note that

$$R = 0.08314 \frac{\text{L bar}}{\text{mol K}}$$

- Relative enthalpies can be determined from heat capacity data and heats of transition.

– Integrate  $C_P(T)$  from  $T_1$  to  $T_2$ , adding in  $\Delta_{\text{fus}}H$  and  $\Delta_{\text{vap}}H$  as necessary.

- **Thermochemistry:** The branch of thermodynamics which concerns the measurement of the evolution or absorption of energy as heat associated with chemical reactions.
- McQuarrie and Simon (1997) reviews exothermic/endothermic reactions, and  $\Delta_r H = H_{\text{prod}} - H_{\text{react}}$ .
- **Hess's Law:** The additivity property of  $\Delta_r H$  values.
- **Standard reaction enthalpy:** The enthalpy change associated with one mole of a specified reagent when all reactants and products are in their standard states. *Denoted by  $\Delta_r H^\circ$ .*
  - An intensive quantity.
- **Standard molar enthalpy of formation:** The standard reaction enthalpy for the formation of one mole of a molecule from its constituent elements. *Denoted by  $\Delta_f H^\circ$ .*
  - We can obtain such values even if a compound cannot be formed directly from its elements via several related reactions and Hess's Law.
- To calculate  $\Delta_r H$  for the general chemistry equation



using standard heats of formation, we decompose the reactants into their component elements in their normal states and then reassemble them into the products.

- Mathematically,

$$\Delta_r H = y\Delta_f H^\circ[\text{Y}] + z\Delta_f H^\circ[\text{Z}] - a\Delta_f H^\circ[\text{A}] - b\Delta_f H^\circ[\text{B}]$$

- The enthalpies of reaction at temperatures  $T_1, T_2$  are related by

$$\Delta_r H(T_2) - \Delta_r H(T_1) = \int_{T_1}^{T_2} \Delta C_P(T) \, dT$$

where

$$\Delta C_P(T) = yC_{P,Y}(T) + zC_{P,Z}(T) - aC_{P,A}(T) - bC_{P,B}(T)$$