PHYSICS 7B: Physics for Scientists and Engineers

Jack Lipson

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Contents

Chapter 0

Syllabus

0.1 Important Info

Syllabus schedule here

0.1.1 Contacts + Sections

Instructor OH:

1. Robert Birgeneau; robertjb@berkeley.edu; Tu 2-3pm
2. Dr.Chen/Giles-Donovan OH are Th 2-3pm.

Lecture 1: MWF 11-12p @ Physics North 1

Head GSI: Yucehn Tang; ytang5@berkeley.edu; begin emails with [7B Lec.1]

2 Sections: DIS + LAB; Labs not every week and may be replaced by DIS (check syllabus)

0.1.2 Materials

1. 7B Workbook by Hedeman (on bCourses)
2. Mastering Physics (Purchase access code)
3. Physics for scientists and engineers 5th edition by Giancoli (may come w/ mastering physics purchase)

0.1.3 Assignments

Homework will be made available Friday 11:59 and due next Friday 11:59.

Must complete all 4 Labs - Sep 29; Oct 27; 11/17; 12/1.

Midterms - Pimentel 1 - 9/25 8-10pm + 10/30 8-10pm.

Final - TBD.

Chapter 17

Temperature, Thermal Expansion, and the Ideal Gas Law

17.1 Atomic Theory of Matter

Definition 1 (Unified Atomic Mass Units (u))**.** We define ^{12}C to have exactly 12.0000 *unified atomic mass units* (u) such that $1\,\mathrm{u} = 1.6605 \times 10^{-27}\,\mathrm{kg}$.

Definition 2 (Elements, Compounds, Atoms, Molecules)**.** *Elements* are substances that cannot be broken down into simpler substances by chemical means, *compounds* are substances made up of elements that can be broken down, *atoms* are the smallest pieces of an element, and *molecules* are the smallest pieces of compounds made up of atoms.

Proposition 1. To convert between Celsius and Fahrenheit, use:

$$T(^\circ\mathrm{C}) = \frac{5}{9}[T(^\circ\mathrm{F}) - 32] \quad T(^\circ\mathrm{F}) = \frac{9}{5}[T(^\circ\mathrm{C}) + 32]$$

Remark. Different materials do not expand precisely linearly over a wide temerpature rage. Thus, we standardize with the *constant-volume gas thermometer*. This thermometer consists of a hollow rigid bulb with a low-pressure gas connected by a thin tube to a mercury manometer. If the height of the mercury tube is adjusted to ensure the gas maintains a constant volume, the new height reached by the mercury is the temperature.

Definition 3 (Freezing/Boiling Point)**.** The *freezing point* of a substance is defined as that temperature at which the solid and liquid phases coexist in equilibirum s.t. there is no net liquid or solid changing into the other one. The *boiling point* is defined analogously for liquid and gas. These temperatures vary with pressure so pressure is specified usually at 1 atm.

Definition 4 (Thermal Equilibrium)**.** Two objects are defined to be in *thermal equilibrium* is, when placed in contact, no net energy flows from to the other, and their temperatures don't change.

Remark. When two systems are in thermal equilibrium, their temperatures are (by definition) equal and no net energy is exchanged.

Definition 5 (0th Law of Thermodynamics)**.** Specifically experiments indicate that **if two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other**.

Proposition 2 (Thermal Expansion)**.** The thermal expansion in length, area, and volume of a material at a fixed pressure due to change in temperature ΔT is approximately given by:

$$\Delta l = \alpha l_0 \Delta T \quad \Delta A = \gamma A_0 \Delta T \quad \Delta V = \beta V_0 \Delta T$$

where α, γ, β denote the material's*coefficient of linear expansion* with unit $(\mathrm{C}^\circ)^{-1}$ and l_0, A_0, V_0 denote its initial length, area, and volume.

Proof. At a certain temperature, a thin rod of length l_0 at temperature T_0 is heated by ΔT to a temperature T. This causes it to expand by Δl to a length l, or $l(T)$, that is dependent on the original length l_0, the temperature change ΔT, and its coefficient of linear expansion α. Thus, $\Delta l = \alpha l_0 \Delta T$ so $l = l_0(1 + \alpha \Delta T)$. For a thin plate with area A_0, this becomes $A = A_0 + \Delta A = A_0(1 + \alpha \Delta T)^2 = A_0 + 2\alpha A_0 \Delta T + \alpha^2 A_0 \Delta T^2$. Thermal expansion for volume is similarly $V = V_0 + \Delta V = V_0(1+\alpha\Delta T)^3 = V_0 + 3\alpha V_0 \Delta T + 3\alpha^2 V_0 \Delta T^2 + \alpha^3 V_0 \Delta T^3$.

Because α and (usually)ΔT are extremely small, we say $\Delta A \simeq 2\alpha A_0 \Delta T$ and $\Delta V \simeq 3\alpha V_0 \Delta T$ implying the coefficient for area $\gamma \simeq 2\alpha$ and the coefficient for volume $\beta \simeq 3\alpha$. □

Note. If water at 0 ℃ is heated, its volume *decreases* until it reaches 4 ℃ when it behaves normally and expands as the temperature increases.

This implies that above 4 ℃ the surface water in a lake/river in contact with cold air sinks because it is denser bringing in warmer water from below causing convection to bring the whole body to the same temperature. As water cools below 4 ℃, however, its volume expands so its density decreases meaning the the surface water turning to ice is less dense than the water below so a layer of ice forms on top. The ice acts as an insulator, allowing life to exist under ice.

Definition 6 (Thermal Stresses). If 2 ends of a material are rigidly fixed, temperature change can cause compressive or tensile stresses called *thermal stresses*.

If the beam tries to expand by $\Delta\ell$ while rigid braces exert a force to hold the beam in place, compressing OR expanding it, the force required is $\Delta\ell = \frac{1}{E}\frac{F}{A}\ell_0$ where E is Young's modulus for the material. Substituting the thermal expansion equation gives the stress to be $\frac{F}{A} = \alpha E \Delta T$.

Definition 7 (State Variables). Quantities detectable by instruments are called *state variables*. For a gas in a container, they are pressure P, volume V, temperature T, and quantity of gas – mass m or equivalently *moles*.

Definition 8 (Mole). One *mole*, abbreviated mol, is defined to be the number of atoms in exactly 12 g of ^{12}C. This number N_A is called *Avogadro's number* and equal to 6.022×10^{23}.

Definition 9 (Equilibrium States). When the state variables of a system are not chaning in time and equal throughout the system.

Definition 10 (Absolute Zero). Absolute zero of temperature is $-273.15\,^\circ\mathrm{C}$ or 0 K on the Kelvin scale s.t. $T(K) = T(^\circ C) + 273.15$.

Proposition 3 (Gas Laws). For a fixed quantity of gas, the following 'laws' are valid (as long as the pressure and density are not too great and the gas is not too close to condensating):

1. (Boyle's Law) [At constant temperature], $P_1V_1 = P_2V_2$ and $P \propto \frac{1}{V}$.
2. (Charles's Law) [At constant pressure], $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ s.t. $V \propto T$.
3. (Gay-Lussac's Law) [At constant volume], $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ s.t. $P \propto T$.

Together these imply $PV \propto T$ so $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$.

Definition 11 ((Equation of State for an) Ideal Gas Law). Of course, once mass is left unfixed, experiments show $PV \propto mT$. Specifically,

$$PV = nRT$$

where n is the number of moles of gas and R is the universal gas constant found to be roughly $8.314\,\frac{\mathrm{J}}{\mathrm{mol.K}} = 0.0821\,\frac{\mathrm{L.atm}}{\mathrm{mol.K}} = 1.99\frac{\mathrm{calories}}{\mathrm{mol\ K}}$.

Remark (Important Remarks for Ideal Gas Law). Always give T in kelvins and P as absolute, rather than gauge, pressure. The equation is less 'ideal' for gases at high pressure/density or near the boiling/condensation point. Recall $1\,\mathrm{L} = 1 \times 10^{-3}\,\mathrm{m}^3$.

Definition 12 (Standard Temperature and Pressure)**.** Standard temperature and pressure, abbreviated STP, implies $T = 273.15K(= 0^\circ\ \mathrm{C})$ and $P = 1.00\,\mathrm{atm} = 1.013 \times 10^5\,\mathrm{Nm}^2 = 101.3\,\mathrm{kPa}$.

Note. $1.00\,\mathrm{mol}$ of gas at STP has $V = 22.4\,\mathrm{L}$.

Remark (Avogadro's Hypothesis)**.** Amedeo Avogadro proposed equal volumes of gas at the same pressure and temperature contain equal numbers of molecules. In other words, he proposed R is the same for all gases.

Definition 13 (Boltzmann constant)**.** Because N_A is constant, we can write $PV = \frac{N}{N_A}RT$ where N is the total number of molecules in a gas. Setting the *Boltzmann constant* $k = R/N_A = 1.38 \times 10^{-23}\,\mathrm{J/K}$ gives $PV = NkT$.

Definition 14 (Ideal Gas Temperature Scale)**.** The *ideal gas temperature scale* is based on the property of an ideal gas that pressure is directly proportional to the absolute temperature. Real gases approach this ideal at very low density. This scale takes points $P = 0$ at $T = 0\ K$ and the *triple point* of water when its solid, liquid, and gas states coexist in equilibrium at $P = 4.58\,\mathrm{torr}$ and $T = 0.01\,^\circ\mathrm{C} = 372.16\ K$.

Definition 15 (Absolute/Kelvin Temperature)**.** The absolute temperature T of a substance is determind by putting that substance in good thermal contact with a constant-volume gas thermometer s.t., at constant volume, $T = (273.16\,\mathrm{K}) \lim P_{tp} \to 0(\frac{P}{P_{tp}})$.

Here, P_{tp} denotes the pressure of the gas in the rigid bulb of the thermometer when placed in water at triple point and P is the pressure in the thermometer when it's in contact with the substance determining T.

Chapter 18

Kinetic Theory of Gases

18.1 The Ideal Gas Law and the Molecular Interpreation of Temperature

Definition 16 (Kinetic Theory)**.** The analysis of matter in terms of atoms in continuous random motion is called *kinetic theory*.

Proposition 4 (Postulates of Kinetic Theory)**.** Under these conditions describing an 'ideal gas', real gases follow the ideal gas law quite closely.

1. There are a large number, N, of molecules, each of mass m, moving in random directions with a variety of speeds.
2. The molecules are, on average, far apart from one another. I.e. their average separation is much greater than their diameter.
3. The molecules obey the laws of classical mechanics and only interact when they collide s.t. the potential energy relating to attractive forces between them is much weaker than the kinetic energy.
4. Collisions with another molecule or the wall of the vessel are perfectly elastic and of very short duration relative to time between collisions.

Proposition 5 (Temperature to Average Kinetic Energy of Molecules)**.** The average translational kinetic energy of molecules in random motion in an ideal gas is directly proportional to the absolute temperature of the gas. In other words, $\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$.

Proof. Take a box of length ℓ and ends of area A filled with an ideal gas. Focus on a single molecule of mass m's collision with one wall. Newton's 2nd and 3rd laws tell us a force $F = \frac{dp}{dt}$ is exerted on the molecule. Because collisions are elastic, its velocity v_x is equal in magnitude so $\Delta p = 2mv_x$. If the molecule takes time Δt to travel 2ℓ to the other wall and back,

$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2\ell/v_x} = \frac{m{v_x}^2}{\ell}$. Recall that although the particle may collide with the tops and sides of the container, its x component doesn't change and neither does its momentum.

We can average the force on a wall due to all the N molecules in the box by $F = \frac{m}{\ell}(v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2)$. Averaging, $\overline{v_x^2} = \frac{v_{x1}^2+v_{x2}^2+\cdots+v_{xN}^2}{N}$ s.t. $F = \frac{m}{\ell}N\overline{v_x^2}$. Because $v^2 = v_x^2+v_y^2+v_z^2 \simeq 3v_x^2$, we let $F = \frac{m}{l}\frac{N\overline{v^2}}{3}$. Thus, the pressure on the wall is $P = \frac{F}{A} = \frac{1}{3}\frac{Nm\overline{v^2}}{A\ell} = \frac{1}{3}\frac{Nm\overline{v^2}}{V} \Rightarrow PV = \frac{2}{3}N(\frac{1}{2}m\overline{v^2})$. From the ideal gas law $PV = NkT$, such that $\frac{3}{2}kT = \frac{1}{2}(m\overline{v^2}) = \overline{KE}$. $\square$

Definition 17 (Thermal Motion). This definition explains the relationship between temperature as a measure of motion of molecules such that random motion of a gas is sometimes called *thermal motion*.

Definition 18 (Root-Mean-Square Speed v_{rms}). To calculate how fast molecules molecules move on average in an ideal gas, we can derive the *root-mean-square speed* $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$.

Remark. It's noteworthy that the average speed $\overline{v} \neq v_{rms}$ necessarily. In fact, for an ideal gas, they differ by about 8%.

Note. $\overline{KE} = \frac{3}{2}kT$ tells us as $T \to 0$, $\overline{KE} \to 0$. However, modern quantum theory tells us this is not true and kinetic energy appraoches a small nonzero minimum.

18.2 Distribution of Molecular Speeds

Definition 19 (Maxwell Distribution of Speeds). In 1859, James Maxwell worked out a formula for the most probable distribution of speeds in a gas with N molecules, that is

$$f(v) = 4\pi N(\frac{m}{2\pi kT})^{\frac{3}{2}}v^2e^{-\frac{1}{2}\frac{mv^2}{kT}},$$

where $f(v)dv$ represents the number of molecules that have speeds between v and $v + dv$ such that $\int_0^\infty f(v)dv = N$.

Definition 20 (Activation Energy). Two molecules may chemically react only if their kinetic energy is great enough to partially penetrate each other. This minimum energy is called *activation energy*. The rate of a chemical reaction is proportional to the number of molecules with energy greater than E_A such that rates increase rapidly with increased temperature.

Example (Determining $\overline{v}$ and$\vec{v_p}$)**.** To find the average speed $\overline{v}$, we must integrate over the product of v and the number $f(v)dv$ which have speed v and divide by N the number of molecules. Thus, $\overline{v} = \frac{\int_0^\infty vf(v)dv}{N} = 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}} \int_0^\infty v^3 e^{-\frac{1}{2}\frac{mv^2}{kT}} dv = 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}}(\frac{2k^2T^2}{m}) = \sqrt{\frac{8}{\pi}\frac{kT}{m}}$.

To find the most probable speed, we need simply find when the slope is 0 such that $\frac{df(v)}{dv} = 4\pi N(\frac{m}{2\pi kT})^{\frac{3}{2}}(2ve^{-\frac{mv^2}{2kT}} - \frac{2mv^3}{2kT}e^{-\frac{mv^2}{2kT}}) = 0$. Solving for v gives $v_p = \sqrt{\frac{2kT}{m}}$.

Note. In summary,

$$v_p \approx 1.41\sqrt{\frac{kT}{m}}, \quad \overline{v} \approx 1.60\sqrt{\frac{kT}{m}}, \quad v_{rms} \approx 1.73\sqrt{\frac{kT}{m}}.$$

18.3 Real Gases and Changes of Phase

Remark. At high pressure, the volume of a real gas is *less* than that predicted by the ideal gas law.

Explanation. This is because ideal gases assume the potential energy originating from attractive forces between molecules to be negligible relative to their kinetic energy. This energy pulls molecules closer together so the volume decreases. At lower temperatures, these forces result in *liquefaction* or *condensation*.

18.4 Vapor Pressure and Humidity

Definition 21 (Critical Point/Temperature)**.** At a certain *critical temperature*, a gas will change to liquid phase if suffieicent pressure is applied. This is also called the *critical point*.

Definition 22 (Gas and Vapor)**.** A substance in a gaseous state *below* its critical temperature is called a *vapor*; above the critical temperature it is called a *gas*.

Remark (Phase Diagram)**.** A *PT Diagram* is often called a *phase diagram* because it compares the different phases of a substance.

Definition 23 (Sublimation)**.** *Sublimation* refers to the process wherein, at low pressures, a solid changes directly into the vapor phases *without* passing through the liquid phase.

18.5 Partial Pressure and Humidity

Remark (Cooling Process). Moleculesi n a liquid roughly follow the Maxwell distribution. Molecules of high speeds in a liquid – i.e. E_A – may leave the liquid temporarily but be pulled back by attractive forces. Only those of highest speed *evaporate*, ultimately decreasing the average speed such that the absolute temperature is less. Kinetic theory, then, predicts evaporation is a *cooling process*.

Definition 24 (Saturated Vapor Pressure). At equilibrium, an equal number of molecules enter the vapor above a liquid and enter the liquid. At this point, the pressure of the vapor is said to be *saturated*.

Remark. The concentration of particular molecules in the gas phase above the liquid will not affect the saturated vapor pressure, but will lengthen the amount of time to reach equilibrium due to collisions.

Remark. Increased temperature increases the saturated vapor pressure of a liquid until it equals the external pressure and *boiling* occurs. Bubbles which indicate a change from liquid to the gas phase are crushed if vapor pressure inside the bubbles is less than the external pressure.

Definition 25 (Partial Pressure). *Partial pressure* is the pressure each gas would exert it it alone were present in a mixture. The *relative humidity* is defined to be the ratio of the partial pressure of water vapor to the saturated vapor pressure of water at a given temperature. If the partial pressureo f water exceeds the saturated vapor pressure, the air is *supersaturated*. This excess water may appear as dew or clouds.

Definition 26 (Dew Point). The *dew point* is when water is cooled s.t. the saturated vapor pressure of water equals its partial pressure.

Note. The pressure P of the amosphere as a function altitude y above sea level is, where P_0 is 1.00 atm:

$$P = P_0 e^{-(\rho_0 g/P_0)y} = P_0 e^{-(1.25\times10^{-4}m^{-1})}$$

18.6 van der Waals Equation of State

Theorem 1 (van der Waals Equation of State). Given gas-dependent constants a and b,

$$(P + \frac{a}{(V/n)^2})(\frac{V}{n} - b) = RT.$$

Proof. To make the ideal gas law more accurate, we now resolve (1) the finite size of molecules in comparison to one another and the container and (2) forces between molecules may be greater than the size of molecules.

Let the molecules in a gas behave like hard spheres of radius r such that the volume molecules can move around in is less than the volume V of the container because the distance between molecules never shrinks below $2r$. Where b is the unavailable volume per mole of gas, replace V in $PV = nRT$ by $(V - nb)$. This relation, $P(\frac{V}{n} - b) = RT$ is called the *Clausius equation of state* and predicts ideal gases have less pressure than real gases. Next, molecules at the edge of the gas leaving towards a wall are slowed by a net attractive force pulling them back in, thus exerting less force and pressure on the wall. We say this pressure is proportionally reduced by the density squared, or $(n/V)^2$, for constant a s.t. $P = \frac{RT}{(V/n)-b} - \frac{a}{(V/n)^2}$ or

$$(P + \frac{a}{(V/n)^2})(\frac{V}{n} - b) = RT.$$

Note that at low densities, van der Waals reduces to the ideal gas law. □

18.7 Mean Free Path

Definition 27 (Mean Free Path)**.** We define the *mean free path*, ℓ_M to be the average distance a molecule travels between collisions such that

$$\ell_M = \frac{1}{4\pi\sqrt{2}r^2(N/V)}.$$

Proof. Suppose the molecules of a gas are hard spheres of radius r. Let the path of one molecule with mean speed $\overline{v}$ be a cylinder of radius $2r$ such that if another molecule's center lies in the cylinder a collision will occur. We can assume for now the other molecules are not moving and the concentration of molecules is N/V. Then, $V_cylinder * N/V$ is the number of collisions that will occur. Over a time Δt, the molecule travels $\overline{v}\Delta t$ so the number of collisions is expected to be $\pi(2r)^2\overline{v}\Delta t(N/V)$. Thus, the average distance between collisions is

$$\ell_M = \frac{\overline{v}\Delta t}{\pi(2r)^2\overline{v}\Delta t(N/V)} = \frac{1}{4\pi r^2(N/V)}.$$

If the other molecules are moving, the number of collisions in Δt actually depends on the *relative* speed $v_rel \approx \sqrt{2}\overline{v}$ of the colliding molecules so

$$\ell_M = \frac{1}{4\sqrt{2}\pi r^2(N/V)}$$

. This of course loses meaning at low densities. □

18.8 Diffusion

Definition 28 (Diffusion)**.** In general, the *diffusing* substance moves from a region where its concentration is high to a region where its concentration is low.

Definition 29 (Fick's Law)**.** Consider a tube of cross-sectional area A containg molecules of increasingly smaller concentration left-to-right. Take a small middle section of tube of length Δx with section 1 on the left and 2 on the right. 1 has more molecules causing greater pressure such that more will strike the boundary into the middle section than from 2. Let J be the rate of diffusion in numbehr of molecules/moles/kg per second. This is proportional, with diffusion constant D to the *concentration gradient* or difference in concentration per unit distance $\frac{C_1-C_2}{\Delta x}$. Thus, $J = DA\frac{C_1-C_2}{\Delta x} = DA\frac{dC}{dx}$. This is *Fick's Law*.

Chapter 19

Heat and the First Law of Thermodynamics

19.1 Heat as Energy Transfer

Remark. An 18-th century model pictured heatflow as movement of a fluid substance called *caloric* which could never be detected. Today, heat, like work, represents a transfer of energy.

Definition 30 (Calorie)**.** A *calorie* (cal) is defined as the amount of heat necessary to raise the temperature of 1 gram of water by 1 Celsius degree. The more often used *kilocalorie* (kcal), or ***C****alorie* is 1000 calories. In the UK, heat is measured through *British thermal units* (Btu) defined as the heat needed to raise the temperature of 1 lb of water by 1 F°. Gas companies use the *therm* defined to be 1×10^5 Btu.

Note (Mechanical Equivalent of Heat)**.** The mechanical equivalent oheat is known as $4.186\,\mathrm{J} = 1\,\mathrm{cal}$. And, $1\,\mathrm{Btu} = 0.252\,\mathrm{kcal} = 1056\,\mathrm{J}$.

Definition 31 (Heat)**.** *Heat* is energy transfered from one object to another because of a difference in temperature.

Definition 32 (Internal/Thermal Energy)**.** The sum total of all the neergy of the molecules in an object is called its *internal/thermal energy*. e.g. 2 objects of equal temperature have more internal temperature than just 1.

For monatomic (one atom/molecule) gas, the internal energy

$$E_{int} = N(\frac{1}{2}\bar{v^2}) = \frac{3}{2}NkT = \frac{3}{2}nRT.$$

If the gas molecules contain more than one atom, the rotaional and vibrational energy of the molecules must also be taken into account.

Remark. Internal energy of real gases, as opposed to ideal gases, also depends on pressure and volume (due to atomic potential energy). Similarly, the internal energy of liquids and solids includes electric potential energy associated with chemical bonds.

19.2 Specific Heat

Definition 33 (Specific Heat)**.** An amount of heat Q put into an object of mass m results, depending on its *specific heat* c, in a temperature change of ΔT such that

$$Q = mc\Delta T.$$

Definition 34 (Closed/Open/Isolated Systems)**.** A *closed system* is one for which no mass enters or leaves, but energy may be exchanged with the environment. Mass may enter or leave in an *open system.* If no energy AND no mass passes its boundaries, a system is *isolated.*

Remark (Energy Conservation for Heat Transfer)**.** Within an isolated system, we can write the energy conservation equation for heat transfer as $\Sigma Q = 0$.

Definition 35 (Calorimetry)**.** *Calorimetry* is a technique which quantitatively measures heat exchange using a *calorimeter* that must be well insulated.

Definition 36 (Bomb Calorimeter)**.** A *bomb calorimeter* measures the thermal energy released when a substance burns to determine their Calorie content. In this calorimeter, a carefully weighed sample is placed with an excess of oxygen in the "bomb" that is then placed in the water of a calorimeter with a fine wire passing into the bomb that ignites the mixture.

19.3 Latent Heat

Definition 37 (Change of Phase)**.** A certain amount of energy is required to change a material's phase.

Definition 38 (Heat of Fusion/Vaporization)**.** The heat required to change 1.0 kg of a substance from the solid to liquid state is called the *heat of fusion*, denoted by L_F. The heat required for the change from liquid to the vapor phase is called the *heat of vaporization* L_V. These are also called the *latent heats* of substances.

The heat involved in a change of phase is written as $Q = mL$ where m is the mass of the substance.

Remark. These latent heats also refer to the amount of heat *released* by a substance when it changes from gas to liquid or liquid to solid.

Remark. At the melting point, the latent heat of fusion does not increase the average kinetic energy (and thus the temperature) of the molecules in a solid, but instead overcomes the potential energy from the forces between molecules. This is the same for vaporization. However, vaporization requires a greater average distance between molecules such that the heat of vaporization is far greater than the heat of fusion for a given substance.

19.4 The First Law of Thermodynamics

Definition 39 (The First Law of Thermodynamics)**.** Because heat is defined to be the transfer of energy due to a difference in temperature, let work be the transfer of energy NOT due to a temperature difference such that, as a general statement of the *law of conservation of energy* $\Delta E_{int} = Q - W$.

Note (Sign Conventions)**.** Because Q is the net heat *added* to the system while W is the net work done *by* the system, we say the following:

1. Heat added is +
2. Heat lost is -
3. Work on system is -
4. Work by system is +

Remark. A full summary of the first law of thermodynamics would include kinetic energy K and potential energy U such that

$$\Delta K + \Delta U + \Delta E_{int} = Q - W.$$

Definition 40 (Idealized Processes)**.** An idealized process carried out at:

1. constant temperature ($\Delta T = 0$) is called *isothermal.*
2. constant heat ($Q = 0$) is called *adiabatic.* (This is the case for well-insulated systems or very rapid processes.)
3. constant pressure ($\Delta P = 0$) is called *isobaric.*
4. constant volume ($\Delta V = 0$) is called *isovolumetric* (or isochoric).

Definition 41 (Isotherms). Curves on a PV diagram at different temperatures are called *isotherms*.

Definition 42 (Quasistatically). A process done slowly enough such that a series of equilibrium states are essentially maintained is called *quasistatically*.

Definition 43 (Heat Reservoir). A body whose mass is so large that, ideally, its temperature does not change significantly when heat is exchanged, is called a *heat reservoir*.

Example. Suppose there is a gas of pressure P inside a cylindrical container of area A and length ℓ fitted with a movable piston.

If our system is just the gas, as it exerts a force $F = PA$ on the piston, the work done by the gas is $dW = \mathbf{F} \cdot d\ell = PAd\ell = PdV$ where $d\mathbf{l}$ is an infinitesimal displacement of the piston.

If the gas was *compressed* so $d\ell$ would point into the gas, its volume would decrease and $dV < 0$. Thus, the work done by the gas would be negative s.t. positive work is being done *on* the gas. For a finite change in volume from V_A to V_B, the work W done by the gas will be $W = \int dW = \int_{V_A}^{V_B} PdV$.

For an quasistatic isothermal expansion of an ideal gas, $P = nRT/V$ for constant T tells us $W = nRT \ln \frac{V_B}{V_A}$. This is the area under the curve between points A and B on a PV diagram.

We can replicate this same change of state from A to B for an ideal gas first isovolumetrically then isobarically. For an ideal gas undergoing an isovolumetric process where we lower the pressure from $P_A \to P_B$, we simply reduce the temperature by letting heat flow out ($dV = 0 \Rightarrow W = 0$ so no work is done). For an ideal gas undergoing an isobaric process taking the volume from $V_A \to V_B$, P is constant at P_B so $W = P_B \Delta V = P_B(V_B - V_A) = \frac{nRT_B}{V_B}(V_B - V_A) = nRT_B(1 - \frac{V_A}{V_B})$. Thus, the total work from A to B in this case was $\frac{nRT_B}{V_B}(V_B - V_A)$ which is quantitatively different from $nRT \ln \frac{V_B}{V_A}$.

Definition 44 (Free Expansion). *Free expansion* is a type of adiabatic process when a gas is allowed to expand in volume without doing any work. Picture 2 well-insulated containers connected by a valve such taht one container has gas while the other is empty. When the valve is open, no heat flows or work is done because no objects are moved so $\Delta E_{int} = Q = W = 0$. E_{int} only depends on T so $\Delta T = 0$ as well.

19.5 Molar Specific Heats for Gases

Remark. Specific heats easily apply to solids and liquids. Gases depend much more on how the thermodynamic process is carried out however. Specific heats are given at constant volume c_V and pressure c_P.

Definition 45 (Molar Specific Heats)**.** Molar specific heats C_V and C_P denote the heat required to raise 1 mol of gas by 1 C° at constant volume and pressure respectively. Thus,

$$Q = nC_V\Delta T \qquad \text{[volume constant]}$$
$$Q = nC_P\Delta T \qquad \text{[pressure constant]}$$

where $C_V = Mc_V$ and $C_P = Mc_P$ where M is the molecular mass of the gas (g/mol).

Remark. Imagine an ideal gas is slowly heated by ΔT, first at constant volume, then constant pressure. In the constant volume process, no work is done since $\Delta V = 0$. Thus all the heat Q_V added goes towards increasing internal energy such that $Q_V = \Delta E_{int}$.

However, in the constant pressure process, work *is* done so the added heat Q_P increases the internal energy and does the work $W = P\Delta V_P$ so $\Delta E_{int} = Q_P - P\Delta V_P$.

Because ΔE_{int} is equal in both processes ($\Delta T_V = \Delta T_P$), $Q_P - Q_V = P\Delta V \Rightarrow nC_P\Delta T - nC_V\Delta T = P(\frac{nR\Delta T}{P})$ from the ideal gas law. This implies $C_P - C_V = R$ which is very accurate to what's obtained experimentally.

Remark. Now, a process done at constant volume on a *monatomic* gas does no work so $nC_V\Delta T = nC_V(T-0) = Q_V = \Delta E_{int} = N(\frac{1}{2}m\overline{v^2}) = \frac{3}{2}nRT$. So $C_V = \frac{3}{2}R$.

Definition 46 (Degrees of Freedom)**.** Here, we denote *degrees of freedom* to mean the number of independent way molecules can possess energy.

Example. For instance, a diatomic molecule has 5 total degrees of freedom. 3 from translational energy (x,y,z) plus 2 from rotaional kinetic energy (not 3 because the axis along the line of the 2 molecules has such small inertia it is negligible).

Definition 47 (Principle of Quipartition of Energy)**.** Energy is shared equally among the active degrees of freedom and each active degree of a molecule has on average an energy equal to $\frac{1}{2}kT$.

Note. This makes sense as diatomic molecules have energy $\frac{5}{2}nRT$ about 5/3 times monatomic molecules without degrees of freedom. Hence their C_V being 5/3 as much. Yet, at extreme low and high temperatures, this diverges such that at low temps, molecules only have translational kinetic energy (3/2). And at high temps, molecules also have vibration as 2 degree of freedom (as if from a spring) such that it has kinetic and potential energy (7/2).

Note. For solids, we maintain this same spring idea such that molecules have potential and kinetic energy to do with vibration in the x, y, z directions implying 6 degrees of freedom.

19.6 Adiabatic Expansion of a Gas

Remark. Take the first law of thermodynamics in an adiabatic process ($\Delta Q = 0$) for an ideal gas such that $dE_{int} = dQ - dW = -dW = -PdV$. For an ideal gas, $\Delta E_{int} = nC_V \Delta T$ tells us $nC_v dT = -PdV$. Taking the differential of the ideal gas law gives $PdV + VdP = nRdT$ so $nC_V(\frac{PdV+VdP}{nR}) + PdV = 0$. Rearranging and $C_V + R = C_P$ gives $C_P PdV + C_V VdP = 0$ or $\frac{C_P}{C_V} PdV + VdP = 0$. Defining $\gamma = \frac{C_P}{C_V}$ and integrating finally gives $\ln(P) + \gamma \ln(V) = \text{constant}$ which simplifies to

$$PV^\gamma = \text{constant}.$$

It's important to note the ideal gas law holds for an adiabatic expansion however PV is clearly not constant implying T must be nonconstant.

19.7 Heat Transfer

Definition 48 (Conduction). Heat *conduction* can be visualized via molecular collisions such that faster molecules at a heated end collide with slower-moving neighbors and transfer kinetic energy. In metals, collisions of free electrons are mainly responsible for conduction.

Remark (Thermal Conductivity). Take a uniform cylinder of cross-sectional area A and length ℓ such that ends with temperatures T_1 and T_2 with heat flow Q over a time interval t gives $\frac{Q}{t} = kA\frac{T_1 - T_2}{\ell}$ where k is the *thermal conductivity* constant characteristic of the material. The rate of heat flow (J/s) is directly proportional to $(T_1 - T_2)/\ell$.

Definition 49 (Thermal Gradient). When k or A cannot be considered constant, we instead take the limit of an infinitesimally thin slab of thickness dx such that our equation becomes $\frac{dQ}{dt} = -kA\frac{dT}{dx}$ where dT/dx is the *temperaute gradient*. Here, the negative sign denotes that heat flow is in direction opposite to the temperature gradient.

Definition 50 (Conductors/Insulators). Substances for which k is very large conduct heat rapidly and are called good thermal *conductors*. When k is small, the substances are called good thermal *insulators*.

Definition 51 (Thermal Resistance). The insulating properties of bulding materials are usually specified by R-values or *thermal resistance*, defined as $R = \frac{\ell}{k}$ for a thickness ℓ of a material. Larger R values imply better insulation.

Definition 52 (Convection). Though liquids and gases are poor conductors of heat, *Convection* is the rapid process whereby heat flows via the bulk movement of molecules over larger distances.

Definition 53 (Forced/Natural Convection). For example, *Forced convection* occurs through a fan blowing air while *natural convection* occurs through hot air rising. Hot air or water (in convection currents) rise from buoyancy because heat causes them to expand, decreasing their relative density.

Definition 54 (Radiation). Radiation is heat transferred over empty space through EM waves. IR wavelengths are mainly responsible for heating the Earth.

Definition 55 (Stefan-Boltzmann equation). The rate at which energy leaves a radiating object is $\frac{Q}{t} = \varepsilon\sigma AT^4$ where σ is the *Stefan-Boltzmann constant* with value $5.67 \times 10^{-8}\,\mathrm{W/m^2 \cdot K^4}$. The factor ε, or the *emissivity*, falls between 0 and 1 and is characteristic of the surface of the radiating material.

Remark. A good absorber is *also* a good emitter. Black and dark objects are good emitters with $\varepsilon \approx 1$.

Example. Take an object of emissivity ε and area A at temperature T_1 surrounded by an environment at temperature T_2. Because both objects radiate energy to each other so the object absorbs energy proportional to T_2^4, the *net* rate of radiant heat flow from the object is given by $\frac{Q}{t} = \varepsilon\sigma A(T_1^4 - T_2^4)$.

Definition 56 (Solar Constant). About 1350 J of energy from the Sun strike Earth's atmospher per second per square meter at right angles to the Sun's rays. This number $1350\,\mathrm{W/m^2}$ is called the solar constant. The atmosphere may absorb as much as 70% of this energy such that an object of emissivity ε with area A facing the Sun absorbs at a rate about $\frac{Q}{t} = (1000\,\mathrm{W/m^2})\varepsilon A\cos(\theta)$ where θ is the angle between the Sun's rays and a line perpendicular to the area A. Seasons result from this "effective area" $\cos(\theta)$ capture.

Definition 57 (Thermography). Diagnostic *thermography* uses a thermograph to scan the body and measure the intensity of infrared radiation to detect areas of high metabolic activity.

Chapter 20

Second Law of Thermodynamics

20.1 name

> **Remark.**

$$
\begin{aligned}
P_1' V_1 &= P_2 V_2 \quad \text{from ideal gas law} \\
P_1' &= \frac{P_2 V_2}{V_1} \\
(P_1 + \frac{a}{(V_1/n)^2})(V_1 - nb) &= (P_2 + \frac{a}{(V_2/n)^2})(V_2 - nb) \quad \text{from VDWE} \\
(P_1 + \frac{a}{(V_1/n)^2}) &= \frac{(P_2 + \frac{a}{(V_2/n)^2})(V_2 - nb)}{V_1 - nb} \\
P_1 &= \frac{(P_2 + \frac{a}{(V_2/n)^2})(V_2 - nb)}{V_1 - nb} - \frac{a}{(V_1/n)^2} \\
P_1 &= \frac{(P_2 + \frac{an^2}{V_2^2})(V_2 - nb)}{V_1 - nb} - \frac{an^2}{V_1^2} \\
P_1 &= \frac{P_2V_2 - P_2nb + \frac{an^2}{V_2} - \frac{an^3b}{V_2^2}}{V_1 - nb} - \frac{an^2}{V_1^2} \\
P_1 &= \frac{P_2V_2}{V_1 - nb} - \frac{P_2nb}{V_1 - nb} + \frac{an^2}{V_2(V_1 - nb)} - \frac{abn^3}{V_2^2(V_1 - nb)} - \frac{an^2}{V_1^2} \\
P_1 - P_1' &= \frac{P_2V_2}{V_1 - nb} - \frac{P_2nb}{V_1 - nb} + \frac{an^2}{V_2(V_1 - nb)} - \frac{abn^3}{V_2^2(V_1 - nb)} - \frac{an^2}{V_1^2} - \frac{P_2V_2}{V_1} \\
\frac{P_1 - P_1'}{P_1} &= \frac{\frac{P_2V_2}{V_1 - nb} - \frac{P_2nb}{V_1 - nb} + \frac{an^2}{V_2(V_1 - nb)} - \frac{abn^3}{V_2^2(V_1 - nb)} - \frac{an^2}{V_1^2} - \frac{P_2V_2}{V_1}}{\frac{P_2V_2}{V_1 - nb} - \frac{P_2nb}{V_1 - nb} + \frac{an^2}{V_2(V_1 - nb)} - \frac{abn^3}{V_2^2(V_1 - nb)} - \frac{an^2}{V_1^2}} \\
\frac{P_1 - P_1'}{P_1} &= \frac{\frac{V_1^2V_2^2(P_2V_2) - V_1^2V_2^2(P_2nb) + V_1^2V_2(an^2) - V_1^2(abn^3) - V_2^2(V_1 - nb)(an^2) - V_1V_2^2(V_1 - nb)(P_2V_2)}{V_1^2V_2^2(V_1 - nb)}}{\frac{V_1^2V_2^2(P_2V_2) - V_1^2V_2^2(P_2nb) + V_1^2V_2(an^2) - V_1^2(abn^3) - V_2^2(V_1 - nb)(an^2)}{V_1^2V_2^2(V_1 - nb)}}
\end{aligned}
$$

This simplifies to:

$$
\begin{aligned}
\frac{P_1 - P_1'}{P_1} &= \frac{V_1^2V_2^2(P_2V_2) - V_1^2V_2^2(P_2nb) + V_1^2V_2(an^2) - V_1^2(abn^3) - V_2^2(V_1 - nb)(an^2) - V_1V_2^2(V_1 - nb)(P_2V_2}{V_1^2V_2^2(P_2V_2) - V_1^2V_2^2(P_2nb) + V_1^2V_2(an^2) - V_1^2(abn^3) - V_2^2(V_1 - nb)(an^2)} \\
\frac{P_1 - P_1'}{P_1} &= 1 - \frac{V_1V_2^2(V_1 - nb)(P_2V_2)}{V_1^2V_2^2(P_2V_2) - V_1^2V_2^2(P_2nb) + V_1^2V_2(an^2) - V_1^2(abn^3) - V_2^2(V_1 - nb)(an^2)}
\end{aligned}
$$

Note that at this point all the units cancel so we have made no mistakes. This equation becomes:

$$
\frac{P_1' - P_1}{P_1} = -1 - \frac{(bP_2V_1V_2^3)n - (P_2V_1^2V_2^3)}{ab(V_1^2 - V_2^2)n^3 + (aV_1V_2(V_1 - V_2))n^2 - (bP_2V_1^2V_2^2)n + P_2V_1^2V_2^3}
$$

Our final percentage is now a very ugly function of n moles. Finally substituting in values gives an equation that we can easily plot on Desmos.