

# Thermodynamics MANUSCRIPT

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## Chapter 1

# Thermodynamics

## 1 Heat and Energy

### Thermodynamic System

A *thermodynamic system* is any collection of parts that permits energy transfer between its members. A closed thermodynamic system allows no energy or material transfer across its boundary. Conversely, an open thermodynamic system does allow such interactions with its environment.

### Temperature

*Temperature* is a scale used for quantifying the amount of ‘hotness’ in a system. We’ll soon build up the vocabulary to create a sophisticated definition of temperature, but it suffices for now to say:

*Temperature is a quantity that eventually becomes the same for two systems after sustained contact.*

Typical temperature scale units, namely Fahrenheit and Centigrade, aren’t defined in fundamental terms of length, space, or time.

### Problem 1

At atmospheric pressure (also known as *standard pressure*), liquid water boils at 212°F and freezes at 32°F. On the centigrade scale, these temperatures are 100°C and 0°C, respectively. Calculate the one temperature at which the Fahrenheit and centigrade scales, assumed linear with temperature, are in agreement. Answer:  $-40^{\circ}\text{F} = -40^{\circ}\text{C}$

### Zeroth Law

Sustained contact between two systems can lead to a state called *thermal equilibrium*, achieved when there is zero net energy flowing between each system. This

idea is also contained in the *zeroth law of thermodynamics*:

*If system A and system B are each in equilibrium with system C, then A and B are in equilibrium with each other.*

### Quasistatic Approximation

The *quasistatic approximation* is the limit when thermodynamic processes occur ‘slowly’ enough such the whole substance maintains instantaneous equilibrium throughout any process.

## 1.1 Matter and Temperature

### Thermal Expansion

The volume of an object is subject to its temperature. Adding heat usually causes the volume to increase, an effect called *thermal expansion*.

Taking a one-dimensional example, consider a thin metal rod of length  $L_0$  and initial temperature  $T_0$ . An external heat source changes the rod’s temperature by  $\Delta T$ , and the length is observed to change by  $\Delta L$ . Restoring the temperature to  $T_0$ , the length restores to  $L_0$ . It follows that a linear ‘law’ for thermal expansion can be written as

$$L = L_0 + \alpha L_0 \Delta T, \quad (1.1)$$

where the parameter  $\alpha$  is the *linear thermal expansion coefficient*, measuring typically around  $10^{-5}$  per degree centigrade. The temperature change  $\Delta T$  may be positive or negative, and the rod expands or contracts, respectively.

Thermal expansion occurs in more than one spatial dimensions. For two dimensions, consider a plate of area  $L_0 \times W_0$ . With a change in temperature, the area of the plate becomes

$$\begin{aligned} A &= L_0 W_0 (1 + \alpha \Delta T)^2 \\ &\approx L_0 W_0 (1 + 2\alpha \Delta T). \end{aligned} \quad (1.2)$$

For small temperature displacements,  $\alpha^2 \Delta T^2$  is a reasonably small contribution to thermal expansion and is ignored to first-order approximation. Thus the area scales linearly with temperature, with effective expansion factor  $2\alpha$ .

For three dimensions, the effective expansion constant is  $\beta = 3\alpha$ . If the volume of the object is  $V_0$ , this means

$$V \approx V_0 (1 + \beta \Delta T). \quad (1.3)$$

#### Problem 2

A circular piece with diameter  $d$  is removed from a room-temperature sheet of aluminum. If the sheet

is heated in an oven, how does the area of the hole change with temperature? Does the hole increase or decrease in area? Answer:  $\Delta A = \pi d^2 \alpha \Delta T / 2$ , increasing.

#### Problem 3

On a cool  $4^\circ\text{C}$  morning, a driver fills his aluminum gasoline tank to the full capacity of 106.0 L. That evening, he checks the fuel level and finds 103.4 L remaining in the tank. The coefficient of volume expansion for gasoline is  $9.5 \times 10^{-4}/^\circ\text{C}$ , and for aluminum is  $7.25 \times 10^{-5}/^\circ\text{C}$ . What was the maximum temperature reached by the fuel tank during the day? Answer:  $32.70^\circ\text{C}$

#### Problem 4

Consider a metal rod having a thermal expansion coefficient that varies with temperature such that  $\alpha(T) = A + BT + CT^2$ . Derive a formula for the length of the material as a function of temperature change. Answer:

$$\Delta L = L_0 (A\Delta T + B\Delta T^2/2 + C\Delta T^3/3)$$

### Thermal Stress

An object confined in space may not be able to physically undergo thermal expansion (or contraction), in which case the object undergoes *thermal stress*.

Suppose a thin metal rod of fixed length  $L_0$  is held between two clamps at temperature  $T_0$  with no initial forces on the ends of the rod. If the temperature changes, the rod ‘wants’ to obey the thermal expansion Equation (1.1), written here as

$$\frac{\Delta L}{L_0} = \alpha \Delta T,$$

where  $\alpha$  is the linear thermal expansion coefficient.

Meanwhile, the Young’s modulus for the rod is defined as  $Y = (F/A)/(\Delta L/L_0)$ , so we write

$$\frac{\Delta L}{L_0} = \frac{F}{AY},$$

where  $F$  is the linear tension in the rod (positive or negative) and  $A$  is the cross-sectional area. Since  $\Delta L$  must be zero, we therefore have

$$\frac{F}{A} = -Y\alpha\Delta T. \quad (1.4)$$

## 1.2 Thermal Energy

The phenomenon of ‘heat’ occurs as a consequence of some type of energy expense: mechanical, chemical, electrical, nuclear, etc. We define *thermal energy*, denoted  $Q$ , as the broad subset of energies and potentials that couple strongly to temperature. Like all other energies in physics, thermal energy must be conserved.

It was known to Sir James Joule (1818-1889) and his contemporaries that the amount of work required to raise the temperature of water is directly proportional to the temperature change. Energy in those days was measured in calories, where one *calorie* is the amount of energy required to raise the temperature of one gram of water by one degree centigrade. (One food calorie, denoted with a capital  $C$ , is 1000 ordinary calories.)

Experiments conducted by Joule revealed that one calorie equals 4.186 energy units in the SI system, also known as Joules. (Note that one *BTU*, or British Thermal Unit, is  $252 \text{ cal} = 1055 \text{ J}$ .)

### Specific Heat

A small thermal energy quantity  $dQ$  transferred to a substance of mass  $m$  (without changing the phase) is linearly proportional to the change in temperature. This means we write

$$c = \frac{1}{m} \frac{dQ}{dT}, \quad (1.5)$$

where the proportionality constant  $c$  is the *specific heat* of the substance. Equation (1.5) can often be integrated in the variable  $T$ , giving a more familiar statement

$$Q = mc\Delta T. \quad (1.6)$$

A typical solid metal has  $c$  around 300 J per kilogram of material per degree centigrade. In the same units, liquid water has  $c = 4187$ , frozen water has  $c = 2108$ , and water vapor has  $c = 1996$ .

### Heat Capacity

The product of mass and specific heat yields the *heat capacity*:

$$C = mc \quad (1.7)$$

Like specific heat, the heat capacity is proportional to Joules per degree centigrade, but the notion of ‘per kilogram of material’ has been multiplied away. Heat capacity refers to the whole object.

## 1.3 Phases of Matter

*Phase* is a term synonymous with ‘state of matter’, used for classifying the overall spatial arrangement and dynamics of the particles in a substance. Common phases of matter are solid, liquid, and gas - but the list doesn’t stop there. More exotic phases such as plasmas and liquid crystals occur in nature (and the laboratory).

The phase of a given substance is chiefly determined by (i) the surrounding temperature, and (ii) the surrounding pressure. This is visualized by using a *phase diagram*, which comes in two flavors:  $PT$  and  $PV$ , standing for a pressure-temperature plot or pressure-volume plot, respectively.

### PT Diagram

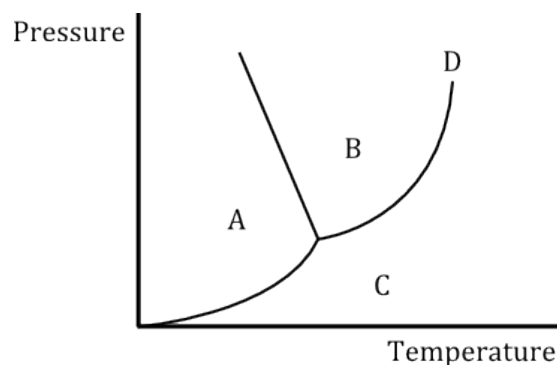


Figure 1.1:  $PT$  phase diagram.

Figure 1.1 illustrates a typical  $PT$  diagram for a typical substance (water for example). A small enough ‘parcel’ of a substance occupies just one point in the phase diagram at a given time, and the parcel’s ‘trajectory’ in a phase diagram is continuous over time, but not necessarily smooth.

Boundaries between regions in the phase diagram are associated with abrupt changes in the phase:

- Region  $A$  has low temperature and high pressure, corresponding to the solid state.
- Region  $B$  has moderate temperature and moderate pressure, corresponding to the liquid state.
- Region  $C$  has high temperature and low pressure, corresponding to the gaseous state.
- Region  $D$  indicates the supercritical state, a phase mixture of liquid and gas.
- Solid lines are boundaries that separate two phases.

- The junction of regions  $A$ ,  $B$ ,  $C$  is called the *triple point*.

### PV Diagram

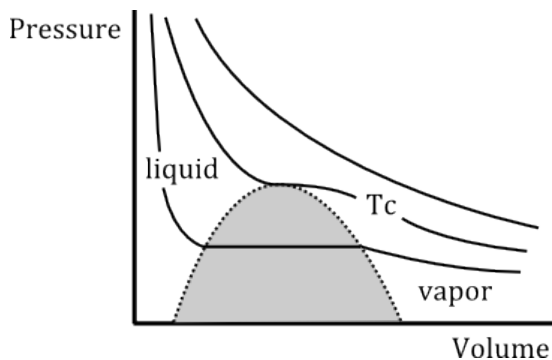


Figure 1.2:  $PV$  phase diagram.

A variation of the  $PT$  diagram is the  $PV$  diagram, where the volume replaces temperature on the horizontal axis. Figure 1.2 illustrates a typical  $PV$  diagram for another typical substance, excluding the solid state. The contour curves are called *isotherms*, having constant temperature. The shaded area under the dotted arch represents the liquid-vapor equilibrium phase. The isotherm  $T_C$  is the *critical temperature*.

### Mixtures and Dalton's Law

A mixture of gases is itself a gas and may be treated as a unit. For instance, if a pressurized vessel holds a mixture of helium and nitrogen, then the gases are fully mixed, sharing the same volume and same temperature.

Each element also makes its own contribution to the pressure, called a *partial pressure*, where the total pressure  $P$  is  $P = P_{He} + P_{Ni}$  for the example on hand. This is known as Dalton's law. In general, the law of partial pressures reads

$$P = \sum_j P_j, \quad (1.8)$$

where index  $j$  sums over the species in the mixture.

### Latent Heat

Changing the temperature or pressure of a substance causes some shift in the phase diagram. Crossing the boundary between any two regions (see Figure 1.1) corresponds to a *phase change*. At such a boundary, molecular order of the substance changes radically, which involves an energy change at the *chemical* level.

Now comes an important point about latent heat. For a substance *on* a phase boundary at a given pressure, all energy added or removed from the substance contributes to phase change with the temperature remaining constant.

To illustrate, consider a glass containing an ice + water mixture having initial temperature  $0^\circ\text{C}$ , the freezing point of water. Placed in a room-temperature environment, the mixture steadily absorbs heat from the surroundings. Does the temperature of the ice + water mixture increase? *No*, not for a while. Rather, any new energy added to the system contributes to melting the ice. Only when the ice is melted will the system's temperature begin to increase. The same experiment works in reverse: if instead the ice + water mixture were placed in a frigid  $-100^\circ\text{C}$  environment, the temperature would remain  $0^\circ\text{C}$  until all liquid water phase changes to ice. Only after this point would the overall temperature begin to plunge. (Of course, this all assumes that water is a perfect conductor of heat.)

During a phase change, the thermal energy of a substance is not governed by  $Q = mc\Delta T$  because  $\Delta T$  is zero during the change. Instead, the change in energy is called *latent heat*, which is proportional to the mass of material being changed:

$$Q = mL_\alpha \quad (1.9)$$

The amount of mass that changes phase per unit energy is a constant denoted  $L_\alpha$ , where subscript  $\alpha$  denotes which phase boundary is being crossed.

Subscript  $\alpha = v$  stands for 'vaporization', corresponding to the liquid-gas boundary, and  $\alpha = f$  stands for 'fusion', corresponding to the solid-liquid boundary. Water at atmospheric pressure has  $L_v = 2.256 \times 10^6 \text{ J/kg}$  and  $L_f = 3.34 \times 10^5 \text{ J/kg}$ .

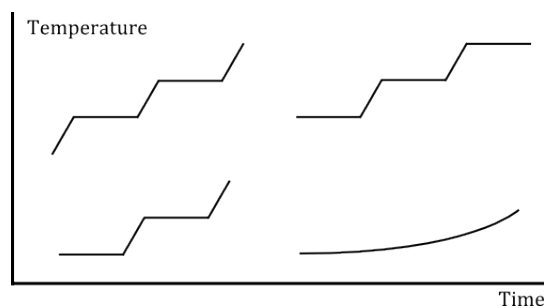


Figure 1.3: Temperature curves for tea kettle problem.

### Problem 5

A tea kettle is filled with ice at  $-10^\circ\text{C}$  and placed on a burner that is steadily getting hotter. Over a long enough time, the kettle empties due to evaporation. Of the four curves drawn in Figure 1.3, which

best represents the temperature inside the kettle as a function of time? Use the quasistatic approximation. Answer: Top-left

#### Problem 6

How much ice at  $0^\circ\text{C}$  must be added to a liter of water at  $80^\circ\text{C}$  so as to end up with all liquid at  $20^\circ\text{C}$ ? Answer:

$$\frac{m_{\text{ice}}}{m_0} = \frac{80^\circ\text{C} - 20^\circ\text{C}}{20^\circ\text{C} + (L_f/c)_{\text{water}}}$$

#### Problem 7

A 15 g ice cube at  $0^\circ\text{C}$  is mixed with 2 g of steam at  $100^\circ\text{C}$  in an isolated container. What is the final state of the system?

Answer: (i) Since  $m_{\text{steam}}L_v - m_{\text{ice}}L_f < 0$ , all steam condenses, releasing 4512 J, which melts 13.51 g of ice, leaving 1.49 g in the solid state. (ii) Next, the 2 g of hot water must come to equilibrium with the melted ice, giving  $0 = 2(x - 100^\circ\text{C}) + 13.51x$ , where  $x$  solves to  $12.9^\circ\text{C}$ . (iii) Finally, let 15.51 g of water at  $12.9^\circ\text{C}$  come to equilibrium with the remaining ice, giving  $0 = 15.51(y - 12.9^\circ\text{C}) + 1.49L_f/c$ . Solving for  $y$ , the final system has 17 g of water at about  $5^\circ\text{C}$ .

#### Problem 8

A 20 g ice cube at  $-10^\circ\text{C}$  is mixed with 2 g of steam at  $100^\circ\text{C}$  in an isolated container. What is the final state of the system?

Answer: (i) Energy required to warm ice to  $0^\circ\text{C}$ : 422 J. (ii) Amount of steam condensed to accomplish this: 0.187 g. (iii) Energy required to melt ice: 6680 J. (iv) Energy released by remaining steam condensation: 4090 J. (v) Energy released from cooling 2 g of water from  $100^\circ\text{C}$  to  $0^\circ\text{C}$ : 837 J. (vi) Energy available to melt ice: 4927 J. (vii) Mass of ice melted: 14.8 g. (viii) Final state has about 5 g of ice and 17 g of water at  $0^\circ\text{C}$ .

## 1.4 Heat Transfer

### Conduction

*Conduction* is heat transfer due to microscopic motions of particles, where more rapidly-moving particles exchange kinetic energy by collision with ‘colder’ particles. A material’s affinity to conduct heat in this way is the *thermal conductivity*,  $k$ , measured in Watts per meter per degree centigrade. (Incidentally, most materials that easily conduct electric currents also have high thermal conductivity.)

Consider two objects  $H$  and  $C$  that are maintained at constant temperatures  $T_H$  and  $T_C$ , respectively. The ‘hotter’ object  $H$  is connected to the ‘colder’ object  $C$  by a conductor having cross-sectional area  $A$  and thermal conductivity  $k$ .

From ordinary classical mechanics, we can write the rate of energy flow  $dQ/dt$  across the conductor:

$$\frac{dQ}{dt} = -\frac{d}{dt} \int \vec{\nabla}U \cdot d\vec{x} = - \int \vec{\nabla}U \cdot \frac{d\vec{x}}{dt}$$

The gradient  $\vec{\nabla}U$  term is proportional to (i) the temperature difference  $\Delta T = T_C - T_H$ , and (ii) the conductor cross section  $A$ . The  $d\vec{x}/dt$  term represents the rate and direction of energy flow across  $A$ , proportional to the thermal conductivity  $k$ . The differential equation for heat conduction is therefore

$$\frac{dQ}{dt} = -kA\Delta T, \quad (1.10)$$

where  $\Delta T$  is known as the *temperature gradient*. The negative sign reminds that heat flows from hot to cold.

### R-Value

The  $R$ -value of a material is equal to the thickness (along the direction of heat flow) divided by the conductivity:

$$R = \frac{L}{k}$$

One inch of wood has  $R \approx 1$ . Typical New England houses have  $R \approx 19$  for the walls and  $R \approx 30$  for the roof. The  $R$ -value is an additive quantity, i.e.  $R_{\text{eff}} = R_1 + R_2 + \dots$

#### Problem 9

The walls of a house are insulated with 2.0 cm of Styrofoam ( $k_{\text{SF}} = 0.01 \text{ W/mK}$ ), and 15.0 cm of fiberglass ( $k_{\text{FG}} = 0.04 \text{ W/mK}$ ). The Styrofoam is on the exterior of the house. The outside temperature is  $0^\circ\text{C}$ , and interior of the house is maintained at  $20^\circ\text{C}$ . (i) Calculate the temperature on the SF-FG interface. (ii) What is the rate of heat transfer per  $\text{m}^2$  through both layers of insulation? (iii) Which provides grater net insulation, an additional 1.0 cm of Styrofoam, or an additional 5.0 cm of fiberglass? Answer:  $6.96^\circ\text{C}$ , 3.5 W, fiberglass.

#### Problem 10

Inside a conductive cylinder of length  $L$  and radius  $R$ , heat flows radially from the axis  $r = 0$  toward the wall at  $R$  with  $T(0) > T(R)$ . Calculate the thermal energy flow rate between any two radii  $r_1$  and  $r_2$  in cylinder. Answer:

$$dQ/dt = k2\pi RL(T_1 - T_2) / \ln(r_2/r_1)$$

#### Problem 11

If a tank of water initially at  $0^\circ\text{C}$  is left in very cold conditions (assume  $-10^\circ\text{C}$ ), a sheet of ice forms on the water surface and grows downward over time.

Supposing all heat transfer takes place through the ice, and not through the container walls: (i) Determine the thickness  $Z$  of the ice as a function of time  $t$ . (ii) Calculate the thickness of the ice sheet that will form in one day. (iii) If the tank is 50 cm deep, how many days does it take to freeze of the water? (iv) If the tank is 10 m deep, how many days does it take to freeze of the water? Answer: (i)  $Z = (\Delta T 2k / (\rho L_f))^{1/2} \sqrt{t}$ , (ii) 9.49 cm, (iii)  $2.40 \times 10^6$  sec, (iv)  $6.40 \times 10^6$  days

### Convection

*Convection* is heat transfer due to macroscopic displacement of a fluid. The displacement can be spontaneous, as when steam carries heat away from a hot cup of tea - or forced, as done inside a refrigerator compressor.

For example, consider a pot of water initially at  $10^\circ\text{C}$  that sits on a kitchen stove burner maintained at  $110^\circ\text{C}$ .

1. Conduction: Heat is introduced to the liquid by contact with the bottom of its metal container, in contact with the heat source.
2. Convection cells: Fluid parcels nudge their way to the surface, spreading horizontally, and submerging when displaced by warmer fluid.
3. Turbulence: The bottom of the fluid becomes much warmer than the surface, and the convection cells burst into mushroom-cloud shapes.
4. Boiling: Discernible patterns vanish, and the fluid expels its heat by ejecting the most energetic particles.
5. Steam: Steam rapidly expands (if not constrained), doing work on the atmosphere.

Steps (2) through (5) each involve convection.

### Electromagnetic Radiation

*Electromagnetic radiation* is energy transfer that uses photons as a carrier. All objects continuously absorb and expel energy through photon exchange with the environment. The net rate of heat flow is given by Stefan's law,

$$\frac{dQ}{dt} = Ae\sigma (T_{\text{obj}}^4 - T_{\text{env}}^4), \quad (1.11)$$

where  $A$  is the object's exposed surface area,  $e$  is the emissivity ( $0 \leq e \leq 1$ ) of the material, and  $\sigma$  is the *Stefan-Boltzmann* constant,  $5.67 \times 10^8 \text{ W m}^{-2} \text{ K}^{-4}$ .

Note the temperature is counted in Kelvin units, which scales proportionally to the centigrade scale but equals zero at  $T = -273.15^\circ\text{C}$ .

A hot electric stove coil emits intense infrared radiation with wavelengths ranging from  $10^3$  nm to  $10^6$  nm. (Your skin easily detects these rays.) With increasing power, the range of emitted wavelengths widens, and eventually the coil visibly glows red with  $\lambda = 700$  nm. (Your eyes easily detect these.) With even more increasing power, the stove coil becomes 'white hot', emitting a very wide spectrum of wavelengths.

A hypothetical object useful for discussing radiation is the *blackbody*, which has  $e = 1$ , absorbing all incident radiation. Contrastly, a *reflector* absorbs no radiation.

#### Problem 12

Earth's upper atmosphere receives roughly  $1.50 \times 10^3 \text{ W/m}^2$  of energy from the sun by thermal radiation. The distance from the earth to the sun is  $1.50 \times 10^{11}$  m, and the radius of the sun  $6.96 \times 10^8$  m. Use conservation of flux to calculate the surface temperature of the sun. Answer: About 6000 Kelvin.

#### Problem 13

*Wandering in the Desert:* Consider an unfortunate person walking at 5 km/h on a hot day in the desert, wearing only a bathing suit. The person's skin temperature tends to rise due to four mechanisms:

- Energy is generated by metabolic reactions in the body at a rate of 280 W, and almost all of this energy is converted to heat that flows to the skin.
- Heat is delivered to the skin by convection from the outside air at a rate equal to  $k' A_{\text{skin}} (T_{\text{air}} - T_{\text{skin}})$ , where  $k'$  is  $54 \text{ J/}^\circ\text{C m}^2\text{h}$ , the exposed skin area  $A_{\text{skin}}$  is  $1.5 \text{ m}^2$ , and the air temperature  $T_{\text{air}}$  is  $47^\circ\text{C}$ .
- The skin absorbs radiant energy from the sun at a rate of  $1400 \text{ W/m}^2$ .
- The skin absorbs radiant energy from the environment, which has temperature  $47^\circ\text{C}$ .

Assume the emissivity of the skin is  $e = 1$  and the skin temperature is  $36^\circ\text{C}$ . (i) Determine the net heat flow into the person due to the four mechanisms. (ii) At what rate (in liters per hour) must perspiration evaporate from the person's skin to maintain a constant skin temperature? (Assume sweat is made of water which has  $L_v = 2.42 \times 10^6 \text{ J/kg}$ .) (iii) Suppose instead that the person is protected by light colored



clothing with  $e = 0$  such that the skin exposed is  $0.45 \text{ m}^2$ . (The convective heat exchange is not affected by the clothing.) What is the rate of perspiration now required? Answer: (i) 280 W, 0.248 W,  $2.10 \times 10^3 \text{ W}$ , 893 W, (ii) 4.87 L/h, (iii) 1.75 L/h

## 1.5 Atmospheric Qualities

### Vapor Pressure

The *vapor pressure* of a substance is the pressure at which the vapor phase is in equilibrium with the solid or liquid phase at a given temperature. For example, water and air in a sealed container will begin mixing by evaporation and condensation (of water molecules in and out of the air). Equilibrium is achieved when the partial pressure  $P_W$  of water *in the air* is equal to the vapor pressure  $P_0$ .

The following table maps out the vapor pressure of water as a function of temperature:

| Temperature<br>(°C) | Vapor Pressure<br>(Pa $\times 10^3$ ) |
|---------------------|---------------------------------------|
| 10                  | 1.23                                  |
| 12                  | 1.40                                  |
| 14                  | 1.60                                  |
| 16                  | 1.81                                  |
| 18                  | 2.06                                  |
| 20                  | 2.34                                  |
| 22                  | 2.65                                  |
| 24                  | 2.99                                  |
| 26                  | 3.36                                  |
| 28                  | 3.78                                  |
| 30                  | 4.25                                  |
| 40                  | 7.34                                  |

Note one Pascal (Pa) is equal to one Newton per square meter.

### Humidity

The *relative humidity* is defined as the ratio

$$H = \frac{P_W}{P_0},$$

always expressed as a percentage and never exceeding 100%. Because Earth's atmosphere is considered open instead of closed,  $H$  is typically much less than unity. On a rainy day,  $H$  becomes close to unity. In either case,  $P_0$  is much less than the atmospheric pressure  $P_A$ , which is near  $10^5 \text{ Pa}$ .

#### Problem 14

At  $24^\circ\text{C}$  and at 50.0% relative humidity, what is the partial pressure of water vapor in the atmosphere? Answer:  $P_W = 1.50 \times 10^3 \text{ Pa}$

#### Problem 15

At  $24^\circ\text{C}$  and at 50.0% relative humidity, what is the mass density of the water vapor in the air? (Hint:  $M = 18 \times 10^{-3} \text{ kg/mol}$ .) Answer:  $\rho = 0.0109 \text{ kg/m}^3$

### Dew Point

Consider an ice-cold glass sitting in a room. After a short time, water droplets form on the outside of the glass. To explain this, observe first that the air surrounding the glass, which itself contains water molecules, is cooled by conduction. The vapor pressure of the surrounding molecules therefore decreases (see table above), causing the relative humidity surrounding the glass to increase. When the relative humidity reaches 100%, the corresponding temperature is called the *dew point*, denoted  $T_{\text{dew}}$ .

At the dew point temperature, *further cooling cannot result in increased humidity*, which is already at unity, so the density of water molecules surrounding the glass must decrease. The excess molecules stick to the glass to form droplets. Note that the dew point is always less than the surrounding room temperature. The higher the relative humidity, the closer the dew point is to the ambient temperature.

#### Problem 16

Suppose the air temperature in a laboratory is  $24^\circ\text{C}$ , and a physics student cools a half-filled drink by adding ice. He finds that water begins to condense on the glass when its temperature reaches  $12^\circ\text{C}$ . What is the relative humidity in the room? Answer: 46.8%

### Clouds and Fog

Clouds and fog are easily explained in the terms defined above. Simply put, condensation (100% relative humidity) occurs at the altitude where the air temperature equals the dew point.

#### Problem 17

Consider a spring day when the air temperature on the ground is  $24^\circ\text{C}$  and the relative humidity is 50%. Assume that the partial pressure of water does not change with elevation, and that the air temperature decreases with altitude at a rate of  $0.06^\circ\text{C}/100\text{m}$ . (i) At what altitude will clouds form? (ii) If the relative humidity on the ground is higher, will the clouds form at a higher or lower altitude? (iii) If the temperature gradient is less, will the clouds form at higher or lower altitude? Answer: (i) 1833 m, (ii) lower, (iii) higher

## 1.6 Ideal Gas

The chain of discoveries leading to the understanding of gases spans across several centuries.

### Boyle's Law

In the seventeenth century, Robert Boyle (1627 - 1691) performed numerous studies on the properties of gases using the materials of his day (simple glassware and metals). The most famous fruit of his effort, called *Boyle's Law*, states that *the pressure of a fixed amount of gas maintained at constant temperature is inversely proportional to the volume of the gas*:

$$P \propto 1/V$$

### Charles's Law

A similar discovery about gases that came out of France in the 1780s, now known as *Charles's Law*, stating that *the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas*:

$$V \propto T$$

### Lord William Kelvin

The linear relationship between volume  $V$  and temperature  $T$  found by Charles has an interesting feature that he probably didn't notice. All experimental data was indicating that any plot that displays  $V(T)$  for *any* substance at *any* pressure has an  $x$ -intercept at  $-273.15^\circ\text{C}$ . Scottish physicist Kelvin realized the significance of this in 1848, and seized the opportunity to name a new temperature scale after himself.

The *Kelvin temperature scale* resembles the centigrade system in every way with one exception: the bottom of the scale, 0 *Kelvin*, corresponds to  $-273.15^\circ\text{C}$ , also known as *absolute zero*. As it turns out, absolute zero is the limit low temperature for any object in the universe.

### Avogadro's Law

Italian scientist Amedeo Avogadro made his contribution in 1811, hypothesizing correctly that *the volume of a gas at constant temperature and pressure is proportional to the number of particles  $N$  composing the gas*:

$$V \propto N$$

### Ideal Gas Equation

Compiling the above achievements into a single equation of state, we arrive at the *ideal gas equation*:

$$PV = NK_B T \quad (1.12)$$

Equation (1.12) describes the macroscopic behavior of all  $N$  particles in a gas at pressure  $P$  and temperature  $T$  (in Kelvin) occupying volume  $V$ . The constant  $K_B$  is the *Boltzmann constant*, and has the experimental value  $1.381 \times 10^{-23} \text{ J/K}$ .

Sometimes in physics (and more often in chemistry) the quantity  $NK_B$  is written instead as  $nR$ , where  $n$  is the number of moles of the gas, and  $R$  is the *ideal gas constant*, measured as  $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$  (Joules per mole-Kelvin).

### Ideal Gas Model

The ideal gas law is an approximate (but usually accurate) description of a realistic gas. As an equation of state, (1.12) holds if the following assumptions can be safely made:

- The volume of the container holding the gas is much greater than the total volume of the constituent gas particles.
- The separation between gas particles is much greater than the diameter of a given particle.
- A given particle's position and direction of travel (not its speed) is completely random.
- Particles do not interact among themselves, with the exception of perfectly elastic collisions.
- The container walls exchange momentum with the gas particles isotropically and don't deform.
- At a given instant,  $P$ ,  $V$ ,  $N$ , and  $T$  are uniform throughout the gas (quasistatic approximation).

Typically, the subscript  $B$  is typically dropped from the Boltzmann constant; thus we simply write  $K$  for now on.

### Problem 18

A rigid box of capacity  $0.5 \text{ m}^3$  is initially open, but is then sealed, trapping air inside at  $20^\circ\text{C}$  at atmospheric pressure. The box is then heated until the pressure inside becomes 3 times that of the atmosphere. Calculate the temperature of the trapped air (in Kelvin) after heating. How many particles are in the box? Answer:  $T = 879.45\text{K}$  and  $N = 1.25 \times 10^{25}$ .

## 2 Kinematic Gas Theory

Consider a sealed rigid vessel of volume  $V$  containing  $N$  non-interacting particles, not necessarily ideal gas. Such a gas has constant pressure and temperature at equilibrium.

### 2.1 Relative Velocity

Of all  $N$  particles in the gas, choose any two of them, where particle '1' has mass  $m_1$  and moves with velocity  $\vec{v}_1$ . Similar can be said for particle '2'. Borrowing from two-body analysis, we can write the kinetic energy of the pair as

$$T = \frac{1}{2}m^*v_{\text{rel}}^2 + \frac{1}{2}(m_1 + m_2)v_0^2,$$

where  $\vec{v}_0$  is the velocity of the center of mass,  $\vec{v}_{\text{rel}}$  is the relative velocity between the particles, and  $m^*$  is the reduced mass. If  $m_1, m_2$  are equal to the same mass  $m$  then  $m^*$  reduces to  $m/2$ .

Starting with the relative velocity

$$\vec{v}_{\text{rel}} = \vec{v}_2 - \vec{v}_1,$$

square both sides and take the average of each term to write

$$\langle v_{\text{rel}} \rangle = \sqrt{\langle v_1 \rangle^2 + \langle v_2 \rangle^2 - 2\langle \vec{v}_1 \cdot \vec{v}_2 \rangle}.$$

If we assume all particles are identical, then the averages  $\langle v_1 \rangle, \langle v_2 \rangle$  are equal to the same velocity  $\langle v \rangle$ . Furthermore, we have that  $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle$  resolves to zero, because all velocity vectors are random and uncorrelated. From this we conclude

$$\langle v_{\text{rel}} \rangle = \sqrt{2}\langle v \rangle,$$

which is to say the average relative velocity between each particle is about 1.41 times the average absolute velocity of the particles in the gas.

### Mean Free Path

Assuming a particle in the gas are spherical with radius  $r$ , the size of a the particle is characterized by the cross-sectional area  $\sigma$  given by

$$\sigma = \pi(2r)^2.$$

In the time  $\Delta t$  between any two collisions, a particle carves out a Gaussian 'tube' of volume

$$V = \sigma \langle v_{\text{rel}} \rangle \Delta t,$$

where  $\langle v_{\text{rel}} \rangle$  is the relative speed between the particle and its target (another particle).

We can also write the collision rate  $f = \Delta N / \Delta t$ . At the least,  $f$  is proportional to the density of the gas  $N/V$ , and is also proportional to the the product  $\sigma \langle v_{\text{rel}} \rangle$ . Thus we write

$$f = \frac{\Delta N}{\Delta t} = \sigma \langle v_{\text{rel}} \rangle \frac{N}{V}.$$

Borrowing from wave mechanics, a frequency  $f$  is associated with a wavelength  $\lambda$  by a velocity term:  $\lambda f = \langle v \rangle$ , and works out to be

$$\lambda = \frac{\langle v \rangle}{f} = \frac{\langle v \rangle}{\sigma \langle v_{\text{rel}} \rangle (N/V)} = \frac{1}{\sigma \sqrt{2}} \frac{V}{N}. \quad (1.13)$$

The distance  $\lambda$  is the *mean free path* for particles of radius  $r$  in the gas. Notice the inverse proportionality to the density and the cross-sectional area. The smaller the particles and the less dense they are, the longer they go before a collision.

### Problem 19

Show that the mean free path for ideal gas molecules is

$$\lambda = \frac{1}{\sigma \sqrt{2}} \frac{KT}{P}.$$

## 2.2 Pressure

We advance on the kinematic gas problem by calculating the pressure in two not so very different ways. For a setup we continue considering a sealed container with volume  $V$  containing gas as temperature  $T$ . Starting from so little, the only freebie we get is that the particle number density is uniform and equal to  $N/V$ . Going forward we'll refer to  $N/V$  as density, but remember there are no mass units involved.

### Heuristic Pressure Calculation

Inside the vessel, consider a cylindrical Gaussian cylinder of length  $L$ , held so the longitudinal  $z$ -axis is perpendicular and adjacent to the inner surface of the vessel with intersection area  $A$ , assumed circular. At any given instant, particles contained in the membrane are moving in all directions.

Question: How many of the particles  $\Delta N$  enclosed in the membrane will collide with the container wall in time interval  $\Delta t$ ? Answer: Statistically half of the enclosed particles collide with the wall (the other half are heading away). A particle will collide with the wall in a time interval  $\Delta t$  if it is heading toward the wall and within a distance  $L = |v_z| \cdot \Delta t$  of the wall, where  $v_x$  is the  $x$ -component particle's absolute speed,  $\sqrt{\langle v^2 \rangle}$ . The collision rate is also proportional

to the overall density of the gas,  $N/V$ . Therefore we may write

$$\Delta N = (1/2) (A |v_z| \Delta t) (N/V) .$$

On any collision with the container wall, there are two contributions to the momentum exchange: (i) the wall first absorbs momentum  $p_z$  to momentarily stop the gas particle, and (ii) the wall then imparts momentum  $-p_z$  to the particle, with a total exchange of  $\Delta p = 2mv_z$  per collision.

By the impulse-momentum theorem  $Fdt = m dv$ , the definition of pressure gives

$$P = \frac{F}{A} = \Delta N \frac{1}{A} \frac{\Delta p}{\Delta t} ,$$

and after inserting what we know about  $\Delta N$  and  $\Delta p$ , we have

$$P = \frac{N}{V} m \langle v_z^2 \rangle .$$

Assuming the gas to be isotropic and living in three dimensions, it follows that

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_z^2 \rangle ,$$

bringing us to the result

$$P = \frac{1}{3} \frac{N}{V} m \langle v^2 \rangle . \quad (1.14)$$

### Problem 20

In a 60 sec interval, 700 hailstones strike a  $0.5 \text{ m}^2$  glass window at an angle of  $45^\circ$  with respect to the normal to the window surface. Each hailstone has mass of 4.0 g and speed 8.0 m/s. If the collisions are purely elastic, Calculate the average force and pressure on the window.

### Formal Pressure Calculation

Inside the vessel, a given particle has any speed between zero and infinity in any direction. Introducing  $f(\vec{v})$  as a generalized velocity distribution, we write the normalization condition as

$$1 = \int_{\text{all } \vec{v}} f(\vec{v}) d^d v ,$$

where  $d$  is the number of dimensions in velocity space.

Performing the prior analysis using more vector language, the same Gaussian cylindrical membrane of length  $L$  inside the vessel touches the inner  $z$ -wall with common area element  $-dA\hat{z}$ , where  $dA = dx dy$ . For particles with speed  $v$  inside the Gaussian cylinder, the length is represented by the vector  $\vec{L} = (dt)\vec{v}$ . The number of particles  $\Delta N$  destined to collide with the wall is proportional to the macroscopic density

$N/V$  times the volume  $d\vec{A} \cdot \vec{L} = dA dt v_z$ . Upon collision, the particle reverses the  $z$ -component of its momentum, with  $dp_z = 2p_z$ . Particles with negative  $p_z$  are heading away from the wall and don't collide.

Collecting these observations, write the 'pressure operator' as

$$[P_v] = \Delta N \frac{dF}{dA} = \Delta N \frac{dp_z/dt}{dA} = \frac{N}{V} v_z 2p_z ,$$

and the total pressure is given by

$$P = \int_{\vec{v}} [P_v] f(\vec{v}) d^3 v ,$$

expanding to:

$$P = \int_{v_x=-\infty}^{v_x=\infty} \int_{v_y=-\infty}^{v_y=\infty} \int_{v_z=0}^{v_z=\infty} \times \frac{N}{V} v_z 2p_z f(\vec{v}) dv_x dv_y dv_z$$

Note the careful choice of limits on the  $v_z$  variable: no particles are coming from outside the container.

Since  $f(\vec{v})$  is an even function by symmetry arguments, it does no harm to integrate over the interval  $-\infty < v_z < \infty$  and divide by a factor of 2. The integral simplifies to

$$P = \frac{N}{V} \int_{\vec{v}} (v_z p_z) f(\vec{v}) d^3 v = \frac{N}{V} \langle v_z p_z \rangle ,$$

where the statistical definition of average has been used. Finally, note again from symmetry that  $3 \langle v_z p_z \rangle = \langle vp \rangle$ , and the pressure takes a form reminiscent of Equation (1.14):

$$P = \frac{1}{3} \frac{N}{V} \langle vp \rangle$$

## 2.3 Effusion

*Effusion* takes place as gas particles are allowed to escape through a small aperture in the enclosing vessel. While the substance is losing particles, energy, and so on - we still work within the quasistatic approximation to gain insight into the phenomenon.

### Effusion Rate

Let us calculate the rate  $R$  (measured in  $\text{s}^{-1}$ ) at which particles that strike a small patch of area  $A$  from inside the vessel. This is analogous to the pressure calculation, however now we ignore momentum exchange. For this, we begin with

$$R = \int_{\vec{v}} [R_v] f(\vec{v}) d^3 v$$

such that

$$[R_v] = A \frac{N}{V} v_z .$$

Expressed in 3D spherical coordinates, the effusion rate is

$$R = \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi/2} \int_{v=0}^{v=\infty} \times \\ A \frac{N}{V} v \cos(\theta) f(\vec{v}) v^2 dv \sin(\theta) d\theta d\phi,$$

where the  $z$ -axis is perpendicular to the container wall on the patch  $A$ . The gas exists only above the  $z = 0$  plane, as indicated by the choice of limits on the variable  $\theta$ . In this coordinate system, it follows that the normalization condition is

$$\int_0^{\infty} f(\vec{v}) 4\pi v^2 dv = 1.$$

Using the statistical definition of average velocity, the instantaneous effusion rate simplifies down to

$$R = \frac{A N}{4 V} \langle v \rangle. \quad (1.15)$$

### Effusion Energy

With the effusion rate known, it's possible to frame the calculation for the average energy per particle carried away by effusion. Begin with the definition of the average energy

$$\langle E \rangle = \int_{\vec{v}} [E_z] f(\vec{v}) d^3v,$$

and use

$$[E_z] = \left( \frac{1}{R} \right) \left( A \frac{N}{V} v_z \right) \left( \frac{m v_z^2}{2} \right).$$

Note that the  $\theta$ -integral resolves via

$$\int_0^{\pi/2} \cos^3(\theta) \sin(\theta) d\theta = \frac{1}{4},$$

and simplify the  $\langle E \rangle$  expression to deduce

$$\langle E \rangle = \frac{m}{4} \frac{\langle v^3 \rangle}{\langle v \rangle}. \quad (1.16)$$

#### Problem 21

Show that the average effusion energy per ideal gas particle is  $\langle E \rangle = KT$ . Explain why the total energy carried away per effused particle is  $2KT$ . Compare with  $3NKT/2$  to explain why the temperature of the vessel holding an effusing gas decreases so rapidly.

## 2.4 Maxwell Speed Distribution

Our recent achievements, namely calculating pressure and effusion quantities, are generally applicable and have not assumed the ideal gas model. To gain special traction on the ideal gas, we borrow from a more general study of Boltzmann factors to write the *Maxwell(-Boltzmann) speed distribution*:

$$D(v) dv = \left( \frac{m}{2\pi KT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2KT} dv \quad (1.17)$$

The chance of finding an ideal gas particle with speed within the interval  $[v_1, v_2]$  equals the area under  $D(v)$  curve spanning that interval, or

$$P(v_1 < v < v_2) = \int_{v_1}^{v_2} D(v) dv.$$

The curve 'opens up' parabolically near speed  $v = 0$ , has a finite peak, and dies off exponentially for very large  $v$ .  $D(v)$  is already normalized such that  $P = 1$  for the interval  $[0, \infty]$ .

Note also there is one dependent variable in  $D(v)$ , but it is indeed a three-dimensional equation: the  $4\pi v^2$  term is byproduct of spherical coordinates in 'velocity space'.

### Average Speed

With  $D(v)$  on hand, we use Gaussian integrals to calculate the average speed  $\langle v \rangle$  for the ideal gas:

$$v_{\text{ave}} = \langle v \rangle = \int_0^{\infty} v D(v) dv = \sqrt{\frac{8KT}{\pi m}} \quad (1.18)$$

#### Problem 22

Use Gaussian integrals to prove the following:

$$\langle v^2 \rangle = \frac{3KT}{m} \\ \langle v^3 \rangle = \frac{4KT \langle v \rangle}{m} \\ \langle v^4 \rangle = \frac{5KT \langle v^2 \rangle}{m}$$

### Maximum Speed

A single derivative of Equation (1.17) determines the peak  $v_{\text{max}}$ :

$$v_{\text{max}} = \sqrt{\frac{2KT}{m}} \quad (1.19)$$

## RMS Speed

The *root mean square* speed is defined as  $\sqrt{\langle v^2 \rangle}$ , or

$$v_{\text{rms}} = \sqrt{\frac{3KT}{m}}. \quad (1.20)$$

Writing each result side-by-side, we see:

$$v_{\text{max}} < v_{\text{ave}} < v_{\text{rms}},$$

or

$$\sqrt{\frac{2KT}{m}} < \sqrt{\frac{8KT}{\pi m}} < \sqrt{\frac{3KT}{m}}$$

The numerical coefficients are approximately 1.414, 1.596, and 1.732 respectively.

### Problem 23

Ideal gas molecules in a container have the following measured speed distribution:

| Speed (m/s) | Percentage |
|-------------|------------|
| 220         | 10%        |
| 250         | 10%        |
| 500         | 15%        |
| 650         | 30%        |
| 900         | 20%        |
| 1300        | 15%        |

Calculate the average speed, the rms speed, and the most probable speed. If the system is ideal gas of molecular mass  $M = 50 \times 10^{-3}$  kg/mol, what is the temperature? Answer: 690 m/s, 768 m/s, 650 m/s, 1180 K

### Problem 24

The escape speed for a particle to leave the gravitational influence of a massive body is given by  $(2GM/R)^{1/2}$ . The temperature near the top of Jupiter's multicolored cloud layer is about 140K. The temperature of Earth's atmosphere at 20km is 220K. Calculate the RMS speed of  $H_2$  molecules in each of those environments. Give the answer as a fraction of the escape speed from the respective planet. Answer: 14.7% for Earth and 2.16% for Jupiter, explaining the rarity of  $H_2$  in Earth's atmosphere. Jupiter's atmosphere consists of 89%  $H_2$  plus other gases.

### Problem 25

Ceres is an asteroid with a mass equal to 0.014 times the mass of the Moon, has density 2400 kg/m<sup>3</sup>, and surface temperature around 200 K. Can this object support an  $O_2$  atmosphere? Answer:  $v_{\text{rms}}/v_{\text{esc}} = 72.9\%$  thus  $O_2$  will largely leave the asteroid.

## 2.5 Equipartition of Energy

### Internal Energy

Assuming gas particles do not mutually interact at a distance, the quantity  $m\langle v^2 \rangle/2$  represents the average internal energy per particle in the system. According to Equation (1.14), we find the general result

$$\langle U \rangle = \frac{m\langle v^2 \rangle}{2} = \frac{3PV}{2N},$$

or, scaling by all  $N$  particles,

$$U = \frac{3}{2}PV, \quad (1.21)$$

where for an ideal gas, the internal energy resolves to

$$U = \frac{3}{2}NKT.$$

Focusing on the factor of 3 momentarily, recall that it arises from symmetry by generalizing to three dimensions from one. Let us further generalize the idea of 'dimension' to mean 'degree of freedom'. That is, point-like gas particles in a box have three translational degrees of freedom. When molecules are *not* point-like, their motions may include rotation and vibration. These modes of motion (unavailable to points or spheres) make new contributions to the internal energy.

For an ideal gas comprised of non-point-like molecules, we will eventually prove the internal energy obeys

$$U = \frac{f}{2}NKT, \quad (1.22)$$

where  $f$  is the number of degrees of freedom available to a given molecule. Note that each degree of freedom must be *quadratic* with respect to its dependent variable. Kinetic energy is  $mv^2/2$ , and similarly rotational and vibrational energies are  $I\omega^2/2$  and  $k\Delta x^2/2$ , respectively.

### Problem 26

Insert the ideal gas Equation (1.12) into the internal energy Equation (1.21) to recover the formula for  $v_{\text{rms}}$ .

### Problem 27

The temperature of 7.00 mol of helium gas, considered ideal, is increased by 2.00 K. What is the change in internal energy?

### Equipartition Theorem

Equation (1.22) is a corollary of a more general statement called the *equipartition theorem*, stating:

*The internal energy per molecule gains a factor of  $KT/2$  for each independent quadratic degree of freedom.*

This theorem can be *derived* in full generality using statistical mechanics (also accounting for non-quadratic potentials), but is beyond the scope of this study.

### Diatomic Molecules

Consider a generalized ideal gas made of  $N$  dumbbell-shaped  $H_2$  molecules. In accordance with (1.22), we count the quadratic degrees of freedom per molecule as follows:

- Three translational modes, so  $f$  is at least 3.
- Two degrees of rotational freedom. The diatomic molecule may spin like a baton in two orthogonal modes, however rotations about the axis joining the atoms do not change during collision. So far,  $f = 3 + 2$ .
- Two contributions from the single vibrational mode (a combination of both kinetic and potential energies), increasing  $f$  again by 2.

We expect therefore that the energy of a diatomic gas is

$$U_{\text{dia}} = (7/2)NKT .$$

However,  $f = 7$  is only observed at high temperatures. Experiments performed on  $H_2$  gas have shown that only translational modes occur at temperatures under 200 K. Below this, the rotational and vibrational energies are ‘frozen out’ and don’t contribute to the internal energy. By 400 K, the two rotational modes are fully active. Vibrational modes finally show themselves around 4000 K. Evidently, diatomic molecules have  $f$  appearing as 3, 5, or 7, depending on  $T$ .

#### Problem 28

Use the equipartition theorem to find the total rotational energy of the molecules in 4.00 mol of diatomic gas at 310 K.

## 2.6 Heat Capacity

The heat capacity is the factor that couples energy change to temperature change for a given substance (not news):

$$C = \frac{dQ}{dT} \quad (1.23)$$

It is generally wrong to assume that *all* added energy contributes to the kinetic energy of the gas, as

some effort is ‘wasted’ on volume expansion of the system. We therefore frame heat capacity calculations somewhere between two extremes: constant volume and constant pressure, where  $C$  gains a respective  $V$ - or a  $P$ -subscript.

### Ideal Gas at Constant Volume

Consider a sample of ideal gas inside a sealed, infinitely rigid container of fixed volume  $V$ . It follows that all added heat contributes to the kinetic energy, as only the pressure and temperature are variable. Using equations (1.22) and (1.23), we find

$$C_V = \frac{f}{2}NK . \quad (1.24)$$

For one mole of monatomic gas with point-like constituents with  $f = 3$  (such as helium or argon), the prediction for  $C_V$  evaluates to

$$C_{V_{\text{mon}}} = \frac{3}{2}R = 12.47 \frac{\text{J}}{\text{mol} \cdot \text{K}} ,$$

in very good agreement with experiments. Due to complications that are later solved by quantum mechanics, Equation (1.24) is only accurate for some gases.

### Ideal Gas at Constant Pressure

For systems allowed to change volume while maintained at constant pressure, the added energy  $\Delta Q$  splits according to

$$\Delta Q = \Delta U_{\text{int}} + P\Delta V ,$$

where the increase in translational, rotational, and vibrational motions of the molecules is all contained in  $\Delta U_{\text{int}}$ , and  $P\Delta V$  is the energy needed to shove the environment out of the way as the gas expands. Taking a  $T$ -derivative of the above yields

$$C_P = C_V + NK , \quad (1.25)$$

where  $P\Delta V/\Delta T$  has been replaced using the ideal gas equation.

### Gamma Factor

The dimensionless ratio  $C_P/C_V$  is called the *gamma factor*, which comes out to

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f} . \quad (1.26)$$

#### Problem 29

Methane ( $CH_4$ ) is a 3-dimensional molecule - a tetrahedron with carbon in the center. Determine the best approximations for  $C_V$  and  $\gamma$ . Answer:  $24.9 \text{ J mol}^{-1}\text{K}^{-1}$  and 1.33

## Elemental Solids

The equipartition theorem allows easy calculation of the heat capacity of many solids. For our purposes, a solid is regarded as a semi-frozen ideal gas, which we take as a periodic arrangement of molecules with no contributions to thermal energy from translational or rotational motions. The structure is held together by quadratic potentials, thus such solids have six degrees of freedom per molecule: three components of kinetic energy due to vibration and three corresponding quadratic potentials.

According to (1.24), one mole of ‘frozen gas’ with  $f = 6$  has

$$C_{V,\text{solids}} = \frac{6}{2}R = 24.9 \frac{\text{J}}{\text{mol} \cdot \text{K}},$$

which is obeyed by *all* elemental solids at high enough temperature, known as the *rule of Dulong and Petit*.

## 2.7 Van der Waals Model

The *van der Waals* model is an extension of the ideal gas law that accounts for the particle size and the interactions between particles. To write a generalized ideal gas law, two experimental constants enter the mix - blandly named  $a$  and  $b$ .

The starting point is the ideal gas model, with equation of state  $PV = NKT$ . Supposing each of  $N$  particles in a sample (gas or liquid) has volume  $b$ , we make the replacement

$$V \rightarrow V - Nb,$$

where the variable  $V$  is understood as the volume available for the sample to occupy. The particles themselves do not contribute to  $V$ .

Next we assume particles interact through the attractive *Leonnard Jones potential*. Without increasing temperature, particle interactions lead to an increase in number density  $N/V$  and pressure  $P$ , as evident by considering a particle on the surface layer of the sample. On the surface layer, the net force on a particle is inward, proportional in strength to  $N/V$ . The total force inward is proportional to the surface area of  $V$ , contributing another factor  $N/V$ . It follows that the correction to pressure is

$$P \rightarrow P + a(N/V)^2,$$

where  $a$  is a constant of dimension  $\text{kg m}^5 \text{s}^{-2}$ .

The van der Waals equation is

$$\left(P + a \frac{N^2}{V^2}\right)(V - Nb) = NKT, \quad (1.27)$$

and is accurate for many types of gases and fluids. Water vapor has  $a = .5507 \text{ J m}^3 \text{mol}^{-2}$  and  $b = 3.04 \times 10^{-5} \text{ m}^3/\text{mol}$ . In the same units,  $N_2$  gas has  $a = .1361$  and  $b = 3.85 \times 10^{-5}$ , and  $H_2$  gas has  $a = .0247$  and  $b = 2.65 \times 10^{-5}$ .

## 3 First Law

### 3.1 First Law of Thermodynamics

Thermodynamic systems are subject to energy conservation as any other mechanical system would. If  $U$  is the internal energy of a substance at pressure  $P$  and volume  $V$ , any thermal energy  $dQ$  added (or removed) must follow

$$dU = dQ - PdV, \quad (1.28)$$

known as the *first law of thermodynamics*.

To make sense of the sign of the  $PdV$  term, imagine adding heat  $+dQ$  to a gas sample using a candle. If the experiment is prepared such that the temperature does not change, making  $dU = 0$ , then the gas necessarily expands its volume. The  $PdV$  term must appear negative to balance out  $dQ$ .

### 3.2 Thermodynamic Processes

A *thermodynamic process* is any change in the state variables characterizing a thermodynamic system. In many cases, only some variables may change, such as temperature and pressure, while other variables remain fixed, such as volume and number of particles. In the following we classify some of the common thermodynamic processes.

#### Isothermal Process

An *isothermal* process is one that leaves the system’s temperature unchanged, which generally means there is no change in the system’s internal energy. The first law with  $dU = 0$  reads  $0 = dQ - PdV$ .

#### Isochoric Process

A process that leaves the system’s volume unchanged (easier said than done) is classified as *isochoric*. The  $dV$  term in the first law is zero by construction, so all heat added to the system contributes to internal energy via  $dU = dQ - 0$ .

#### Isobaric Process

A process that leaves the system’s pressure unchanged (easily said and easily done) is classified as



*isobaric*. For example, the macroscopic work done on a gas is not an integral  $\int PdV$ , but simply the product  $P\Delta V$ .

### Adiabatic Process

*Adiabatic* processes are those that have zero net heat transfer into or out of the system. The first law of thermodynamics quantifies this by  $dU = 0 - PdV$ , where any internal energy change  $dU$  is balanced out by response in pressure and volume.

### Reversible Processes

Many processes in classical mechanics (oscillations, orbits, etc.) are *reversible*, where the system may backtrack along its path in configuration space by reversing time  $t \rightarrow -t$  without violating any laws of physics or probabilistic expectations. Only *some* thermodynamic processes are reversible, and only if conditions are right, with one example being isothermal phase change between water and ice at  $0^\circ\text{C}$  in a sealed container.

In reality, thermodynamic phenomena are naturally *irreversible*, such as when a bomb explodes, or when scrambling an egg. Witnessing either of these in reverse would be extremely unlikely. To restore such a system to its original state, an external reorganizing force would have to intervene.

## 3.3 Ideal Gas Processes

We now examine the consequences of thermodynamic processes for a controlled sample of ideal gas, always obeying the ideal gas Equation (1.12).

### Isothermal

For isothermal expansion in ideal gas, the total energy entering the gas equals the total work done on the environment, given by the integral

$$W = \int PdV = \int_{V_i}^{V_f} \frac{NKT}{V} dV,$$

simplifying to

$$W = NKT \ln \left( \frac{V_f}{V_i} \right). \quad (1.29)$$

That is, all added heat contributes to volume expansion.

### Isochoric

An isochoric process permits no volume change, which we studied when writing the heat capacity of ideal gas at constant volume. The first law tells us  $dQ = dU$ , where meanwhile we know  $dQ/dT = C_V = fNK/2$ . It follows that the work done during an isochoric process is

$$W = C_V \Delta T = \frac{f}{2} NK \Delta T. \quad (1.30)$$

### Isobaric

For an ideal gas, we found  $C_P = C_V + NK$ , leading to

$$W = C_P \Delta T = \left( \frac{f}{2} + 1 \right) NK \Delta T. \quad (1.31)$$

### Adiabatic

An adiabatic process usually involves a rapid expansion or compression of a gas that is ‘too fast’ for external heat transfer, making  $dQ = 0 = dQ - PdV$ . Inserting the ideal gas internal energy relation (1.22) into the first law, we write a differential equation

$$\frac{f}{2} dT = -T \frac{dV}{V}, \quad (1.32)$$

implying:

$$\begin{aligned} PV^\gamma &= \text{constant} \\ TV^{\gamma-1} &= \text{konstant} \end{aligned} \quad (1.33)$$

The work entering an ideal gas during an adiabatic process is

$$W = \int P dV = NK \int \frac{T}{V} dV = NK \frac{f}{2} (T_i - T_f),$$

simplifying to

$$W = -\frac{PV}{T} \frac{f}{2} \Delta T. \quad (1.34)$$

Note the term  $(PV/T)$  may be evaluated at *any* point during the adiabatic process, so long as the combination of  $P$ ,  $V$ , and  $T$  are known simultaneously. Using relation (1.26), we may alternatively write

$$W = \frac{1}{1-\gamma} (V_f P_f - V_i P_i). \quad (1.35)$$

The variable  $\gamma$  is always  $> 1$  by construction, thus (1.35) has a buried negative sign. If the *overall* sign of  $W$  is positive, the work is done *by* the gas. If negative, the work is done *on* the gas.

### Free Expansion of Ideal Gas

Consider a sealed, perfectly-insulating vessel with ideal gas contained within half of its total volume. The other half of the vessel is vacuum, and a thin membrane separates the two compartments. The membrane is then punctured and the gas is allowed to freely expand into the vacuum until the two compartments are in equilibrium. (The system is not quasistatic during expansion.)

Such free expansion is an adiabatic process, as no heat enters or leaves the vessel through the insulated walls. The system does zero work, as no force is required to expand into vacuum. The temperature change is zero according to Equation (1.34), thus the internal energy change is also zero. In summary, we see

$$Q = W = \Delta T = \Delta U = 0,$$

showing the energy state of the gas is unchanged. Of course, the gas will never accidentally find itself crammed into one side of the box again; work *would* be required to compress the system to its original state. Free expansion of ideal gas is therefore irreversible.

#### Problem 30

Take a  $P$ -derivative of Equation (1.33) to derive

$$\frac{dT}{dP} = \frac{2}{f+2} \frac{T}{P}. \quad (1.36)$$

#### Problem 31

Consider an ideal gas of  $N$  particles with initial temperature  $T_i$  and initial volume  $V_i$  that is compressed to final volume  $V_f$ . Which process requires more energy compress the gas, isothermal or adiabatic?

#### Problem 32

At height  $z$  in the Earth's atmosphere, (i) show that a horizontal thin layer of air with (massless) volume density  $\rho(z)$  and pressure  $P(z)$  in obeys the equation  $dP/dz = -mg\rho(z)$  at mechanical equilibrium, where  $m$  is the average mass of molecules in the air. (ii) Consider a bubble of gas that moves upward fast by expanding or shrinking adiabatically. Show that the temperature gradient experienced by the bubble is given by

$$\frac{dT}{dz} = -mg\rho(z) \frac{2}{f+2} \frac{T}{P}.$$

(iii) At low altitudes above sea level, the pressure decreases by about 1.2 kPa for every 100 m. For higher altitudes within the troposphere, show that

$$P(z) = P_0 e^{-mgz/KT_0},$$

where  $P_0$  and  $T_0$  are measured at sea level ( $P_0 \approx 101325$  Pa,  $T_0 \approx 288.15$  K).

#### Problem 33

A scuba diver is swimming a depth of 25 m where the pressure is 3.5 atm. The air she exhales forms bubbles 8.0 mm in radius, which rise to the surface where the pressure is 1 atm. Assume the bubbles remain at the uniform 300 K temperature of the surrounding water. How much work is done by each bubble as it expands to the rising surface? Answer: 0.953 J

#### Problem 34

When a quantity of monatomic ideal gas expands at a constant pressure of  $4.00 \times 10^4$  Pa, the volume of the gas increases from  $2.00 \times 10^{-3} \text{ m}^3$  to  $8.00 \times 10^{-3} \text{ m}^3$ . (i) What is the change in internal energy of the gas? (ii) Does heat flow into out of the gas? (iii) What is the magnitude of the heat flow? Answer: 360 J, 600 J into the gas.

## 3.4 Thermodynamic Cycles

A *thermodynamic cycle* is a chain of processes that bring an open system's state variables to a previous configuration. It follows that the net internal energy change  $\Delta U$  is zero for a complete thermodynamic cycle, meaning that any heat added to a system must be removed somewhere in the same cycle.

During any infinitesimal volume change, work done is equal to  $PdV$ . Integrated over a thermodynamic cycle, the total work done equals the area enclosed by the loop on the  $PV$  diagram. If the loop traces out in a clockwise direction, the work output of the system is positive. When going counterclockwise, the system absorbs work over a complete cycle.

### Heat Engine

A *heat engine* is a device that utilizes a thermodynamic cycle in repetition to perform 'useful' work. The *efficiency* of a heat engine is defined as the ratio of output work over input heat energy. Using the first law we write

$$e = \frac{W}{Q_H} = \frac{Q - \Delta U}{Q_H} = \frac{Q}{Q_H}. \quad (1.37)$$

Through a complete thermodynamic cycle, the net heat flow  $Q$  equals  $Q_H + Q_C$ . The efficiency is therefore

$$e = \frac{Q_H + Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right|,$$

using the fact that  $Q_C$  is negative for a typical heat engine.

Problem 35

Two moles of an ideal diatomic gas are taken around the cycle  $abc$  as shown in Figure 1.4. Data:  $P_a = 1.00 \times 10^5 \text{ Pa}$ ,  $P_c = 1.40 \times 10^5 \text{ Pa}$ ,  $V_a = 0.049 \text{ m}^3$ . If the path from  $b$  to  $c$  is isothermal, calculate the work done by the gas. Answer:  $-2300 \text{ J}$

Problem 36

Two moles of an ideal diatomic gas are taken around the cycle  $abc$  as shown in Figure 1.4. Data:  $P_a = 1.00 \times 10^5 \text{ Pa}$ ,  $P_c = 1.40 \times 10^5 \text{ Pa}$ ,  $V_a = 0.100 \text{ m}^3$ . If the path from  $b$  to  $c$  is adiabatic, calculate the volume of the gas at point  $c$ . Answer:  $0.13 \text{ m}^3$

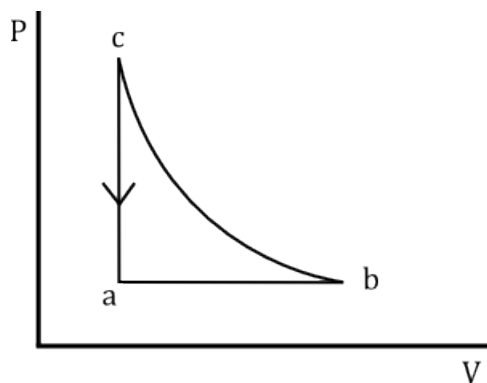


Figure 1.4:  $PV$  diagram showing thermodynamic cycle.

Problem 37

A cylinder with a piston contains  $0.150 \text{ mol}$  of nitrogen at  $1.80 \times 10^5 \text{ Pa}$  at  $300 \text{ K}$ . The nitrogen may be treated as an ideal diatomic gas whose molecules can rotate, but not vibrate. The gas is first compressed isobarically to half its original volume. It then expands adiabatically back to its original volume, and is finally heated isochorically to its original pressure. (i) Do the arrows on the corresponding  $PV$  diagram point clockwise or counterclockwise? Draw it. (ii) Compute the temperatures at the beginning and end of the adiabatic expansion. (iii) Compute the minimum pressure. (iv) Compute the work done by nitrogen during one thermodynamic cycle. Answer: (i) counterclockwise, (ii)  $150 \text{ K}$ ,  $114 \text{ K}$ , (iii)  $6.82 \times 10^4 \text{ Pa}$ , (iv)  $-75 \text{ J}$

**Otto Cycle**

Many automobiles operate on the gasoline-burning *Otto cycle*. Inside Otto engines, a fuel-air mixture (approximately ideal gas) is compressed inside a piston and then ignited with a spark, resulting in rapid volume expansion to ‘blast’ the piston outward, applying work that ultimately reaches the wheels. The spent fuel-air mixture is ejected from the piston and

the process repeats. Engines in general have a different number of steps required to complete their thermodynamic cycles, with popular conventions being ‘two-stroke’ and ‘four-stroke’.

The Otto cycle consists of four thermodynamic processes illustrated in Figure 1.5. We begin analyzing an Otto engine piston as it is fully expanded at volume  $V_{\text{max}}$  and filled with a fuel-air mixture (approximately ideal gas), ready to ignite. In this ‘cool’ state, the piston has temperature is  $T_0$  pressure  $P_0$ .

1. Compression stroke (adiabatic): An external force (work left over from a previous cycle) rapidly compresses the piston to volume  $V_{\text{min}}$ . The pressure of the fuel-air mixture thereby increases to  $P_1$ , and the temperature increases to  $T_1$ . Because no significant heat is added to the cylinder during the compression stroke, it is an adiabatic process.
2. Fuel ignition (isochoric): With the piston fully compressed, a spark ignites the fuel-air mixture, quickly releasing a great deal of kinetic energy  $Q_H$  into the gas. The pressure jumps quickly to  $P_2$ , and likewise the temperature to  $T_2$ . The volume remains constant at  $V_{\text{min}}$ . The energy added follows the relation:

$$Q_H = nC_V (T_2 - T_1) ,$$

where  $n$  is the number of moles of fuel-air mixture in the piston.

3. Power stroke (adiabatic): The cylinder’s volume expands to  $V_{\text{max}}$  following ignition, and whatever device is attached to the moving part of the piston receives organized work  $W$  (driving the car forward, for instance). The pressure drops to  $P_+$  during this process, but not quite down to  $P_0$ . The spent fuel-air mixture is still ‘hot’ at this point, having temperature  $T_+$ , slightly greater than  $T_0$ .
4. Exhaust stroke (isochoric): The cylinder expels the spent fuel-air mixture of energy  $Q_C$  to the environment and takes in a new fuel-air packet, returning the pressure to  $P_0$ . The piston effectively remains at  $V_{\text{max}}$  (after intake of new fuel), and is ready again for a compression stroke. The (negative) energy added follows the relation

$$Q_C = nC_V (T_0 - T_+) .$$

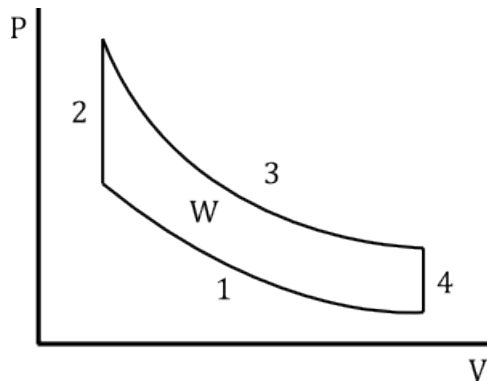


Figure 1.5: Otto cycle.

The efficiency of the Otto engine is straightforward to calculate by Equation (1.37), giving

$$e = 1 + \frac{Q_C}{Q_H} = 1 + \frac{T_0 - T_+}{T_2 - T_1},$$

but we can do better. The Otto cycle's two adiabatic transitions obeys Equation (1.33), allowing all  $T$ -variables to cancel. Meanwhile, define the piston *compression ratio*  $r = V_{\max}/V_{\min}$  so the formula for  $e$  boils down to

$$e = 1 - \frac{1}{r^{\gamma-1}}. \quad (1.38)$$

#### Problem 38

How much of  $Q_C$  may be used to bolster to the power stroke of an engine? Answer: None, not even theoretically.

#### Problem 39

A gasoline engine takes in  $8.00 \times 10^3$  J of heat and delivers  $1.60 \times 10^3$  J of work per cycle. The heat is obtained from gasoline with a heat combustion of  $4.6 \times 10^4$  J/g. (i) What is thermal efficiency? (ii) How much heat is discarded in each cycle? (iii) What mass of fuel is burned in each cycle? (iv) If the engine goes through 70.0 cycles per second, what is the power output in watts? (v) What is the power in horsepower? Answer: 0.212,  $6.70 \times 10^3$  J,  $1.85 \times 10^{-4}$  kg,  $1.62 \times 10^5$  W, 217 hp.

#### Problem 40

A Toyota Celica GT has a four cylinder Otto-cycle engine with a compression ratio of  $r = 9.50$ . The diameter of each cylinder, called the *bore* of the engine is 87.1 mm. The distance that the piston moves during the compression, called the *stroke* of the engine is 90.9 mm. The initial (and minimal) pressure of the air - fuel mixture (when the volume is maximal) is  $8.50 \times 10^4$  Pa, and the initial temperature is 300 K (same as the environment). Assume that 200J of heat

is added to each cylinder in each cycle by burning the fuel (gasoline), which has  $C_V = 20.5 \text{ Jmol}^{-1}\text{K}^{-1}$  and  $\gamma = 1.40$ . (i) Calculate the work done in each cycle. (ii) Calculate the thermal energy released when the gas is cooled to the temperature of the outside air. (iii) Calculate the minimal volume of the air - fuel mixture. (iv) Calculate  $P$ ,  $V$ , and  $T$  just before ignition. Answer: 119 J, 81.3 J,  $6.05 \times 10^{-4} \text{ m}^3$ ,  $1.99 \times 10^6$  Pa,  $6.37 \times 10^{-5} \text{ m}^3$ , 738 K

#### Diesel Cycle

Some automobiles and nearly all road shipping vehicles (excluding hybrid drives) operate on the *diesel cycle*. Like the Otto cycle, the diesel cycle entails four thermodynamic processes. Inside a diesel engine piston however, fuel-air mixture (approximated as ideal gas) is compressed until it self-ignites without the help of a spark, causing the power stroke. The ignition takes place in a constant-pressure condition, and the volume jumps almost instantly, much unlike the Otto cycle's ignition scenario.

#### Problem 41

Figure 1.6 is the  $PV$  diagram for the diesel cycle. The compression stroke, the instant of fuel ignition, power stroke, and exhaust stroke are labeled 1, 2, 3, 4, respectively. Assuming steps 1 and 3 are adiabatic, show that the efficiency of the diesel engine is given by

$$e = 1 - \frac{1}{\gamma} \frac{(c/b)^{-\gamma} - (c/a)^{-\gamma}}{(c/b)^{-1} - (c/a)^{-1}},$$

where volumes  $a$ ,  $b$ , and  $c$  are indicated on the horizontal axis and  $\gamma$  is the ratio  $C_P/C_V$ .

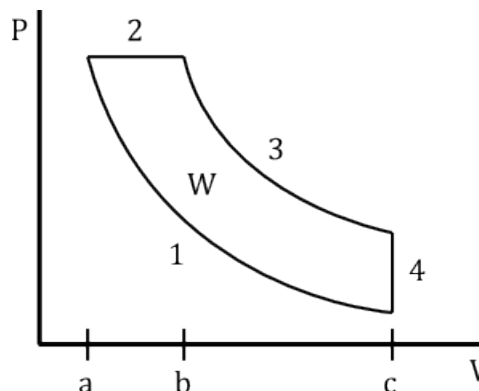


Figure 1.6: Diesel cycle.

### Refrigerators

A refrigerator operates as a heat engine in reverse: work is required to displace heat from the cold reservoir to the hot reservoir. The working substance that circulates inside a refrigerator is a fixed amount of water, freon, or ammonia (no chemical exhaust). The operation is outlined as follows:

1. Starting in the gaseous phase, the working substance is forced through a compressor, emerging with reduced volume and increased temperature and pressure.
2. The substance goes through a long heat-conducting tube called the *condenser*, which is in thermal contact with the environment (hence the refrigerator needs to ventilate). In the condenser, the working substance loses heat  $Q_H < 0$  and changes phase to liquid.
3. The working substance then encounters a very small ‘bottleneck’ called the *throttle* that hinders most of the circulation. On the input side of the throttle, the temperature and pressure of the working substance are relatively high. The output side is at much lower temperature and pressure.
4. As a cold liquid, the working substance passes through the refrigerator body, warming again to the gaseous phase, absorbing energy  $Q_C > 0$ .

Like the heat engine, the refrigerator obeys the first law

$$Q_H + Q_C = Q_{in} = \Delta U + W,$$

where  $\Delta U = 0$  and  $W < 0$ . The merit of a refrigerator is not its efficiency, but instead the *coefficient of performance*, defined as the ratio of heat removed from the refrigerator body over the work required to do so. That is,

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}. \quad (1.39)$$

#### Problem 42

An ideal air conditioner takes heat from a room at 68.5°F and transfers it to the environment, which is at 93.1°F. For each joule of electrical energy required to operate the air conditioner, how many joules of thermal energy are removed from the room?

#### Problem 43

Liquid refrigerant at a pressure of  $1.34 \times 10^5$  Pa leaves the expansion valve of a refrigerator at  $-22^\circ\text{C}$ .

It then flows through the vaporization coils inside the refrigerator and leaves as vapor at the same pressure at a temperature of  $-18^\circ\text{C}$ , the same temperature as the inside of the refrigerator. The boiling point of the refrigerant at this pressure is  $-18^\circ\text{C}$ , the heat of vaporization is  $1.60 \times 10^5$  J/kg, and the specific heat capacity of the vapor is  $485 \text{ Jkg}^{-1}\text{K}^{-1}$ . The coefficient of performance of the refrigerator is  $K = 2.52$ . If 8.00 kg of refrigerant flows through the refrigerator each hour, find the electric power that must be supplied to the refrigerator. Answer: 123 W

#### Problem 44

A heat pump designed for southern climates extracts heat from the outside air, and delivers air at  $20^\circ\text{C}$  to the inside of the house. Compute the coefficient of performance of the heat pump (i) in the south, where the outside temperature is  $5^\circ\text{C}$ ; (ii) in the north, where the outside temperature is  $-10^\circ\text{C}$ . (iii) Two identical houses, one in the north and one in the south, are heated by this pump, and maintain temperatures of  $20^\circ\text{C}$ . Considering heat loss through the walls, windows, and roof, what is the ratio of the electrical power required to heat the two houses? Answer: (i) 18.5, (ii) 8.77, (iii) 4.0

### Carnot Cycle

Sadi Carnot (1796-1832) designed an engine with maximal efficiency by using only reversible isothermal and reversible adiabatic processes. All heat transfer during the Carnot cycle occurs on isotherms; there is no heat transfer across finite temperature differences. No machine using the Carnot cycle would be ‘fast’ enough for industrial standards, but Carnot engines are still the most efficient type.

The gaseous working substance within a Carnot engine piston never leaves the piston, and undergoes no chemical change. Carnot engines rely on a literal ‘hot’ reservoir from which to draw energy, and a similar ‘cold’ reservoir to deposit energy. These two reservoirs may in practice be as simple as hot and cold containers of water. The four stages of the Carnot cycle go as follows:

1. Slow isothermal: A piston in the ‘compressed’ state enclosing a gas of volume  $V_{\min}$  is attached to a reservoir at high temperature  $T_H$  and absorbs heat  $Q_H$  isothermally. The volume swells to  $V_1$ , and the reservoir is removed. Recall from Equation (1.29) that

$$Q_H = NKT_H \ln \left( \frac{V_1}{V_{\min}} \right).$$

2. Fast adiabatic: The gas expands adiabatically, lowering its temperature from  $T_H$  until it reaches  $T_C$ . The volume swells once more to reach a maximum  $V_{\max}$ .
3. Slow isothermal: The system moves to contact the cold reservoir of temperature  $T_C$ , where isothermal compression takes the volume to  $V_2$  (with  $V_2 < V_1$ ). The discarded energy is

$$Q_C = -NkT_C \ln \left( \frac{V_{\max}}{V_2} \right).$$

4. Fast adiabatic: The system moves away from the cold reservoir and the gas is compressed adiabatically, raising its temperature from  $T_C$  until it reaches  $T_H$ . The volume returns to  $V_{\min}$ .

The efficiency of the Carnot engine, according to definition (1.37), is

$$e = \frac{Q_H + Q_C}{Q_H} = 1 - \frac{T_C \ln(V_{\max}/V_2)}{T_H \ln(V_1/V_{\min})},$$

where Equation (1.33) for adiabatic processes tells us  $V_{\max}/V_2 = V_1/V_{\min}$ , and thus

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H}. \quad (1.40)$$

Astonishingly, the efficiency depends on neither the construction of an engine nor the properties of the working substance, only the reservoir temperatures:

$$e = 1 - \frac{T_C}{T_H} \quad (1.41)$$

#### Problem 45

Consider a Carnot engine operating between temperatures  $T_H$  and  $T_C$ , where  $T_C$  is above the ambient temperature  $T_0$ . A second engine operates between the temperatures  $T_C$  and  $T_0$ . Show that the overall efficiency of this system is equal to the efficiency of a single Carnot engine operating between  $T_H$  and  $T_0$ .

#### Problem 46

A Carnot engine operating between two thermal reservoirs has an efficiency of  $e$ . When it is run in reverse, it becomes a Carnot refrigerator. Calculate the coefficient of performance. Answer:  $(1 - e)/e$

### Reversible Loops

By riding isothermal and adiabatic curves, Carnot successfully identified a closed loop in the PV diagram that is entirely reversible. It should follow that we may consider any reversible path as a stack of

Carnot cycles. To capture this idea, write Equation (1.40) in the form

$$\frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0$$

where a path made of many isothermal and adiabatic segments must obey

$$\sum \frac{Q}{T} = 0.$$

Heat transfer on shared isotherms cancel, and the sum refers only to the boundary of the PV-curve. Taking a finer resolution, the sum generalizes to a path integral

$$\oint \frac{dQ}{T} = 0. \quad (1.42)$$

Evidently, there is *something* that links quantity  $dQ/T$  to the reversibility of thermodynamic processes.

## 4 Second Law

### 4.1 Entropy

The *entropy* of system is a quantity representing its ‘reversibility’. First surfacing in Equation (1.42), let us define the entropy as

$$S = \int \frac{dQ}{T}. \quad (1.43)$$

For reversible processes, the entropy can be found by direct integration of the above. For two states linked by an irreversible process, it suffices to calculate the entropy over some other path (in the PV diagram) consisting of reversible process that would connect those two states.

#### Problem 47

When 1.00 kg of water at 0°C is frozen to make ice, what is the entropy change? Answer:  $-1200 \text{ J/K}$

#### Problem 48

An object of mass  $m_1$ , specific heat  $c_1$ , and temperature  $T_1$  is placed in contact with a second object mass  $m_2$ , specific heat  $c_2$ , and temperature  $T_2 > T_1$ . As a result, object 1 heats to temperature  $T$  and object 2 cools to  $T'$ . (i) Show that energy conservation requires that  $m_1 c_1 (T - T_1) = m_2 c_2 (T_2 - T')$ . (ii) Show that the entropy increase of the system is

$$\Delta S = m_1 c_1 \ln(T/T_1) + m_2 c_2 \ln(T'/T_2).$$

### Isothermal Expansion of Ideal Gas

For isothermal expansion of ideal gas, we wrote the energy entering the system as Equation (1.29), implying  $\Delta Q = NKT \ln(V_f/V_i)$ . By the definition of entropy, it follows that

$$S = NK \ln \left( \frac{V_f}{V_i} \right). \quad (1.44)$$

### Isochoric Expansion of Ideal Gas

For isochoric expansion of ideal gas, we wrote the energy entering the system as Equation (1.30), implying  $dQ/dT = C_V$ . By the definition of entropy, it follows that

$$S = \int \frac{dQ}{dT} \frac{dT}{T} = C_V \ln \left( \frac{T_f}{T_i} \right). \quad (1.45)$$

### Isobaric Expansion of Ideal Gas

For isobaric expansion of ideal gas, we wrote the energy entering the system as Equation (1.31), implying  $dQ/dT = C_P$ . By the definition of entropy, it follows that

$$S = \int \frac{dQ}{dT} \frac{dT}{T} = C_P \ln \left( \frac{T_f}{T_i} \right). \quad (1.46)$$

### Adiabatic Process in Ideal Gas

Starting with the definition of entropy, an adiabatic process in ideal gas obeys

$$\begin{aligned} S &= \int \frac{dQ}{T} = \int \frac{dU + PdV}{T} \\ &= NK \int \left( \frac{f}{2} \frac{dT}{T} + \frac{dV}{V} \right) = 0, \end{aligned}$$

which evaluates to zero because the terms inside the integral are equal and opposite by Equation (1.32).

### Free Expansion of Ideal Gas

In discussing the free expansion of ideal gas, we found that no energy changes whatsoever, i.e.,  $\Delta U = \Delta Q = W = 0$ . However, we also found that ideal gas expansion is irreversible, so the entropy shouldn't be zero.

To calculate the entropy of free expansion of ideal gas, imagine the effort required to isothermally compress the gas to its original volume. This is precisely the same condition that gave us Equation (1.44), thus the entropy is

$$S = NK \ln \left( \frac{V_f}{V_i} \right).$$

A change in entropy implies a change in the 'quality' of the energy in a system. This means ideal gas freely-expanding through a hole, as opposed to escaping into a vacuum, could instead be used to do something that keeps energy 'organized', such as to wind up a spring connected to a turbine.

### Entropy of Light

A 'gas' of photons, also referred to as blackbody radiation, is subject to entropy. Recall that Stefan's law (1.11) states that the rate of electromagnetic energy transfer is given by

$$\frac{dQ}{dt} = A\sigma (T_{obj}^4 - T_{env}^4),$$

where  $e = 1$  and for simplicity we'll take  $T_{env}$  to be constant. The total energy in a volume  $V$  of photon gas is

$$Q = \frac{\sigma}{c} (T_{obj}^4 - T_{env}^4) \int d^3x = \frac{V\sigma}{c} (T_{obj}^4 - T_{env}^4),$$

and it follows that  $dQ = (V\sigma/c)4T_{obj}^3 dT$ . Thus the entropy  $S$  as a function of  $T_{obj}$  is

$$S = \int \frac{dQ}{T} = \frac{4V\sigma}{c} \int T^2 dT = \frac{4V\sigma}{3c} (T_{obj}^3 - T_0^3).$$

If we approximate  $T_{env} = 0$  and  $T_0 = 0$ , the entropy becomes

$$S = \frac{4}{3} \frac{Q}{T}.$$

## 4.2 Second Law of Thermodynamics

The *second law of thermodynamics* is a restriction on the entropy of closed systems. The following statements more-or-less equally capture the second law:

### Entropy statement

*The entropy of a closed system can never decrease. The entropy of an open system can be forced to decrease, but the net entropy of the system + surroundings necessarily increases.*

### Engine statement

*It is impossible for any system to undergo a cyclic process in which it absorbs heat at a single temperature and converts the heat completely into mechanical work.*

### Refrigerator statement

*It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.*

### 4.3 Systems in Contact

Systems placed in contact will exchange energy, temperature, particles, and so on - depending on the intimacy of contact. Such conjoined systems always tend toward some kind of equilibrium state, and we take advantage of this to re-understand the notion temperature, pressure, etc.

#### Thermal Equilibrium

Consider two thermodynamic systems  $A$  and  $B$  that are in separate, rigid, sealed containers. With  $T_A > T_B$  initially, the systems are then placed in contact to allow internal energy exchange by conduction or radiation, with the total  $U = U_A + U_B$  remaining constant.

A heat packet  $dQ = -dU_A = dU_B$  exchanged between systems changes the entropy of both:

$$dS_A = -\frac{|dQ|}{T_A}$$

$$dS_B = \frac{|dQ|}{T_B}$$

To accommodate the temperature terms, the entropy loss of the hotter system  $A$  is *smaller* in magnitude than the entropy gain of the cooler system  $B$ . The sum  $dS_A + dS_B$  is necessarily positive, thus the energy exchange is irreversible. *Thermal equilibrium* is achieved when the entropy stops increasing, corresponding to  $T_A = T_B = T$ , or

$$\frac{1}{T} = \frac{dS_A}{dU_A} = \frac{dS_B}{dU_B} = \frac{1}{T}.$$

#### Definition of Temperature

Given the the role of entropy in thermal equilibrium, we seize this opportunity to actually *define* the notion of temperature as an entropy maximum with respect to internal energy (for fixed  $V$  and  $N$ ):

$$T = \left( \frac{\partial S}{\partial U} \right)_{V,N}^{-1} \quad (1.47)$$

#### Mechanical Equilibrium

Supposing the partition between systems  $A$  and  $B$  were made flexible but not porous, the systems tend toward *mechanical equilibrium*, where maximum entropy corresponds to equal pressures. Supposing  $T_A = T_B$  with  $V_A > V_B$  initially, the heat packet exchanged between systems is purely mechanical as  $dQ = -P_A dV_A = P_B dV_B$ .

Using the same arguments as above, we may replace instances of  $dQ$  with  $PdV$  terms to get:

$$\frac{P}{T} = \frac{dS_A}{dV_A} = \frac{dS_B}{dV_B} = \frac{P}{T}$$

Alas, we're in position to relate pressure to entropy as we did the temperature. The equation

$$P = T \left( \frac{\partial S}{\partial V} \right)_{U,N} \quad (1.48)$$

describes systems with fixed internal energy and fixed number of particles. Note that the above is merely a tool for calculation, not a refined definition of pressure.

#### Diffusive Equilibrium

We now let systems  $A$  and  $B$  exchange both energy and particles through a non-flexing porous membrane. Placed in contact, the systems achieve *diffusive equilibrium* in addition to thermal equilibrium.

The heat  $dQ$  exchanged between systems is proportional to the number of particles  $dN$  that move across the membrane. The proportionality factor between energy and particles is called the *chemical potential*, denoted  $\mu$ , as

$$dQ = \mu dN.$$

implying

$$\frac{-\mu}{T} = \frac{dS_A}{dN_A} = \frac{dS_B}{dN_B} = \frac{-\mu}{T}.$$

We thus define the chemical potential in terms of the entropy:

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V} \quad (1.49)$$

The minus sign in Equation (1.49) reminds us that particles flow from regions of higher  $\mu$  to lower. When there are multiple particle species present in a system,  $\mu$  adopts a subscript  $i$  for each species, and the quantity  $\mu dN$  becomes  $\sum \mu_i dN_i$ .

### 4.4 First Thermodynamic Identity

Recall the first law of thermodynamics as stated in Equation (1.28), namely

$$dU = dQ - PdV.$$

Our study of thermal and diffusive equilibrium has shown  $dQ$  coming in two flavors as  $dQ = TdS$  and  $dQ = \mu dN$ , respectively. It follows that the first law has a special form

$$dU = TdS - PdV + \mu dN, \quad (1.50)$$

which we'll call the *first thermodynamic identity*.



### Entropy of the Universe

The whole universe consists of any given system plus its total environment such that  $S_{\text{uni}} = S_{\text{sys}} + S_{\text{env}}$ . It follows that Equation (1.50) lets us write:

$$dS_{\text{uni}} = dS_{\text{sys}} + \left[ \frac{1}{T} (dU + PdV - \mu dN) \right]_{\text{env}} \quad (1.51)$$

## 5 Thermodynamic Variables

### 5.1 Free Energies

The meaning of the term *thermal energy* or *thermodynamic potential* can vary depending on the conditions surrounding a system. The distinction is characterized by the *free energy* of the system.

#### Enthalpy

In order to create a system of volume  $V$  that has internal energy  $U$  in an environment at pressure  $P$ , the total energy required is called the *enthalpy*, defined as

$$H = U + PV. \quad (1.52)$$

Enthalpy is the internal energy of a system plus the work required to shove the environment out of the way in order to make room the system. Conversely,  $H$  is the total energy recovered if you could annihilate the system.

The differential enthalpy is  $dH = dU + PdV + VdP$ , where substituting the first thermodynamic identity (1.50) gives a new identity

$$dH = TdS + VdP + \mu dN, \quad (1.53)$$

indicating that a system with fixed  $S$ ,  $P$ , and  $N$  will minimize the enthalpy. The ‘entropy of the universe’ Equation (1.51) accordingly boils down to:

$$dS_{\text{uni}} = -\frac{1}{T} (dH)_{S,P,N}$$

#### Problem 49

Show that the enthalpy of an ideal gas is  $H = 5NKT/2$ .

#### Helmholtz Free Energy

A system of  $N$  particles created in isothermal conditions at constant volume shall borrow energy from the environment (easing the job of the assembler) equal to  $TS$ , where  $T$  is the temperature and  $S$  is the entropy of the system. The net work required is therefore

$$A = U - TS, \quad (1.54)$$

the *Helmholtz Free Energy*, equivalent to the energy recovered if the system is destroyed in the same constant-temperature and constant-volume conditions.

The differential Helmholtz free energy is  $dA = dU - TdS - SdT$ , where substituting (1.50) gives another identity

$$dA = -SdT - PdV + \mu dN. \quad (1.55)$$

In accordance with (1.51), we find that a system with fixed  $V$  and  $N$  in an environment with constant  $T$  will minimize the Helmholtz free energy:

$$dS_{\text{uni}} = -\frac{1}{T} (dA)_{T,V,N}$$

#### Gibbs Free Energy

In conditions where both temperature and pressure are constant, creating a system requires the *Gibbs free energy*

$$G = U + PV - TS, \quad (1.56)$$

which means you supply the internal energy  $U$  and the work  $PV$  to shove the environment out of the way. The environment supplies  $TS$  for you, hence the minus sign. In constant  $T$  and  $P$  conditions,  $G$  is the energy recovered if the system is annihilated.

Taking the differential Gibbs free energy and substituting (1.50) gives a corresponding identity:

$$dG = -SdT + VdP + \mu dN \quad (1.57)$$

At constant temperature and pressure, the  $dT$ - and  $dP$ -terms are zero, leaving us with  $dG = \mu dN$ , which integrates to

$$G = \mu N. \quad (1.58)$$

You might wish that a similar relation connects  $A$  to  $N$  by starting with  $\mu = (\partial A / \partial N)_{T,V}$ . However, adding particles while maintaining fixed  $T$  and  $V$  forces the density to slowly increase, which directly changes  $\mu$ .

A system with fixed  $T$ ,  $P$ , and  $N$  will do whatever it can to minimize the Gibbs free energy, as reinforced by Equation (1.51) applied to this scenario:

$$dS_{\text{uni}} = -\frac{1}{T} (dG)_{P,T,N}.$$

Recall if  $T$  is allowed to vary, the system instead minimizes the enthalpy instead.

### Grand Free Energy

One more grouping of terms useful for describing irreversible processes in open systems is the *grand free energy*, defined as

$$\Phi = U - TS - \mu N . \quad (1.59)$$

The quantity (1.59) is the energy recovered by reducing the system to zero size: putting all particles and energy back into the reservoir. Using Equation (1.58), it's straightforwardly shown that

$$\Phi = -PV . \quad (1.60)$$

Suppose a system of fixed  $V$  is allowed to exchange both  $U$  and  $N$  with its environment. Assume the chemical potential  $\mu$  of the system is already in equilibrium with the environment, as is the temperature  $T$ . The differential version of  $\Phi$  reads

$$d\Phi = dU - TdS - \mu dN ,$$

which is the right hand side of Equation (1.51). It immediately follows that

$$dS_{uni} = -\frac{1}{T} (d\Phi)_{T,V,\mu} ,$$

meaning a system with fixed  $V$  in thermal and diffusive equilibrium with the environment will minimize the grand free energy.

### Internal Energy

A handy consistency check on the internal energy  $U$  can be derived in terms of  $TS$ ,  $PV$  and  $\mu N$ , avoiding terms like  $H$ ,  $A$ ,  $G$ , and  $\Phi$ . Start with the first thermodynamic identity

$$dU = TdS - PdV + \mu dN ,$$

and ask: which potential could be added to  $dU$  in order to make the right side a total derivative? Denoting such a term  $\Xi$ , we write

$$d(U + \Xi) = d(TS) - d(PV) + d(\mu N) ,$$

where clearly,

$$d\Xi = SdT - VdP + d\mu N .$$

Notice though that this is (minus) the differential version of  $\Phi + PV$ , which is identically zero, meaning that  $\Xi$  is exactly zero. Integrating the above gives

$$U = TS - PV + \mu N ,$$

the familiar formula for the Gibbs free energy.

### Gibbs-Duhem Equation

The arrangement of thermodynamic state variables that gives zero on either side of the equation gives a special result relating differential chemical potentials. Begin with the Grand free energy as given by (1.59), and add the  $PV$  term onto the left to get zero on the right:

$$\Phi + PV = U - TS - \sum_i \mu_i N_i + PV = 0$$

Note this discussion applies to a multi-species system, as indicated by the sum over particles with their corresponding chemical potentials. Taking the differential version, we find

$$d(\Phi + PV) = -SdT + VdP - \sum_i d\mu_i N_i = 0 ,$$

where for conditions of constant temperature and constant pressure, we arrive at the *Gibbs-Duhem* equation:

$$\sum_i d\mu_i N_i = 0 \quad (1.61)$$

## 5.2 Legendre Transform

We have found that the energy state of a system is beholden to its (sometimes controlled) relationship with the environment. For example, at fixed temperature, volume, and number of particles, the best representation is the Helmholtz free energy  $A(T, V, N)$ . Here we address *why* to ever bother with different potentials - that is, why not simply write  $U = U(T, V, N)$  and deal with internal energy all the time?

Staying in the Helmholtz regime, to assign  $U$  as a function of  $T$  is patently incorrect, as temperature is already defined by Equation (1.47), namely

$$T = \left( \frac{\partial S}{\partial U} \right)_{V,N}^{-1} .$$

It *is* appropriate however to express the internal energy in terms of the entropy instead as  $U = U(S, V, N)$ . To proceed, consider a given point  $P$  on a  $U(S)$  curve, and determine the slope  $\partial U / \partial S = T$  at that point. Draw a straight line through point  $P$  having slope  $T$ , and extend the line until it hits the  $U$ -axis. The  $U$ -intercept is precisely the Helmholtz free energy  $A$ . That is, we have drawn the line

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

which is equivalent to the usual formula  $A = U - TS$ . Subtracting  $TS$  from  $U$  in this way is called the *Legendre transform*. A similar procedure extends to each of the thermodynamic potentials.

### 5.3 State Variables as Derivatives

Thermodynamic identities (1.50), (1.53), (1.55), and (1.57) can be arranged to express certain state variables. Following are only several of the common relations:

#### Derivates of Helmholtz

$$\begin{aligned} -S &= \left( \frac{\partial A}{\partial T} \right)_{V,N} \\ -P &= \left( \frac{\partial A}{\partial V} \right)_{T,N} \\ \mu &= \left( \frac{\partial A}{\partial N} \right)_{T,V} \end{aligned}$$

#### Derivates of Gibbs

$$\begin{aligned} -S &= \left( \frac{\partial G}{\partial T} \right)_{P,N} \\ V &= \left( \frac{\partial G}{\partial P} \right)_{T,N} \\ \mu &= \left( \frac{\partial G}{\partial N} \right)_{T,P} \end{aligned}$$

#### Derivates of Entropy

$$\begin{aligned} \frac{1}{T} &= \left( \frac{\partial S}{\partial U} \right)_{V,N} \\ \frac{P}{T} &= \left( \frac{\partial S}{\partial V} \right)_{U,N} \\ -\frac{\mu}{T} &= \left( \frac{\partial S}{\partial N} \right)_{U,V} \end{aligned}$$

#### Heat Capacity

$$\begin{aligned} C_V &= \left( \frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2}NK \\ C_P &= \left( \frac{\partial H}{\partial T} \right)_{P,N} = \frac{5}{2}NK \end{aligned}$$

#### Thermal Expansion

As a partial derivative, the coefficient of thermal expansion, namely  $\beta = 3\alpha$  from Equation (1.3) may be written as

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P.$$

A similar property of matter is the isothermal compressibility  $\kappa_T$ , defined as

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T.$$

#### Problem 50

Assume some equation of state (not necessarily the ideal gas equation) connects a system's pressure  $P$ , temperature  $T$ , and volume  $V$ . For the infinitesimal change  $P \rightarrow P + dP$ ,  $T \rightarrow T + dT$  with  $V$  fixed, (i) show that  $(\partial V/\partial P)_T dP + (\partial V/\partial T)_P dT = 0$ . (ii) Next show that

$$\frac{dP}{dT} = \left( \frac{\partial P}{\partial T} \right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}.$$

#### Problem 51

Near room temperature, liquid water has a thermal expansion coefficient  $\beta = 2.5 \times 10^{-4} \text{ K}^{-1}$  and isothermal compressibility  $\kappa_T = 4.5 \times 10^{-10} \text{ Pa}^{-1}$ . Estimate the pressure that must be exerted on a drop of water in order to prevent it from expanding while increasing from  $20^\circ\text{C}$  to  $30^\circ\text{C}$ . Use this result to explain why it is easier to measure  $C_P$  rather than  $C_V$ . Answer: 55.8 atm

#### Problem 52

For a van der Waals fluid obeying Equation (1.27) at fixed  $T$  and  $N$ , use the thermodynamic identity (1.57) to show that the Gibbs free energy is:

$$\begin{aligned} G &= -NKT \ln(V - Nb) \\ &\quad + \frac{N^2 bKT}{V - Nb} - \frac{2aN^2}{V} + C(T) \end{aligned} \quad (1.62)$$

### 5.4 Maxwell Relations

A trick from calculus allows a deeper relationship between derivatives and state variables. Consider a function  $f$  of two variables  $x$  and  $y$ . It's easy to see that the mixed second derivatives of  $f$  are identical:  $\partial_{xy}f = \partial_{yx}f$ . Applying this to thermodynamics, take for example the differential Helmholtz free energy,  $dA$ , with a fixed number of particles. By Equation (1.55), we have

$$dA = -SdT - PdV.$$

From the rules of partial derivatives,  $dA$  also reads

$$dA = \left( \frac{\partial A}{\partial T} \right)_V dT + \left( \frac{\partial A}{\partial V} \right)_T dV,$$

where from calculus, we must have

$$\left( \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial T} \right)_V \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right)_T \right)_V$$

Substituting state variables for the inner derivatives, but leaving the outer ones, we arrive at a *Maxwell relation*:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (1.63)$$

In the same spirit, we can do the same for  $dU$ ,  $dH$ , and  $dG$ , where the number of particles is fixed in all cases. Respectively, the results are:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (1.64)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (1.65)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (1.66)$$

## 5.5 Extensive and Intensive

All variables in thermodynamics fall into one of two classifications. A quantity may be *extensive*, where the scale of the variable goes with the size of the system, or it may be *intensive*, where the scale of the variable doesn't care about the scale of the system. To illustrate, consider a thermodynamic system with the laundry list of state variables. If the system is duplicated and attached to itself, which variables duplicate, and which don't? You should conclude:

**Extensive:**  $M, V, N, U, A, G, S$

**Intensive:**  $P, T, \mu, \rho$

Properties of intensive and extensive variables:

- An extensive quantity multiplied by an intensive quantity yields an extensive quantity.
- The sum of two extensive quantities is also extensive.
- A ratio of extensive quantities yields an intensive quantity.
- The product of two extensive quantities is rare in calculations - check twice if you encounter this.
- The sum of an extensive quantity and an intensive quantity should never arise.

## 6 Chemical Physics

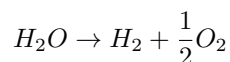
### 6.1 Thermochemistry Tables

In response to change, a thermodynamic system's state variables will adjust in accordance with environmental conditions. At 'standard' room temperature (298 K) and at 'standard' atmospheric pressure (1 atm), also known as *STP* conditions, the enthalpy  $H$ , entropy  $S$ , and Gibbs free energy  $G$  of common substances behave as listed in the following *thermochemistry table*, also called an entropy table:

| Symbol | Species          | Enthalpy<br>$\Delta H$<br>[kJ mol <sup>-1</sup> ] | Entropy<br>$S$<br>[J mol <sup>-1</sup> K <sup>-1</sup> ] | Gibbs free energy<br>$\Delta G$<br>[kJ mol <sup>-1</sup> ] |
|--------|------------------|---|--|--|
| $H_2O$ | Liquid Water     | -285.83   | 69.95  | -237.15  |
| $H_2O$ | Water Vapor      | -241.83   | 188.84   | -228.59  |
| $H_2$  | Hydrogen Gas     | 0   | 130.7  | 0  |
| $O_2$  | Oxygen Gas       | 0   | 205.07   | 0  |
| $O$    | Monatomic Oxygen | 249.170   | 161.055  | 231.731  |
| $N$    | Nitrogen Gas     | 472.704   | 153.298  | 455.563  |
| $NH_3$ | Ammonia          | -45.90  | 192.77   | -16.37   |

### Electrolysis of Water

Consider a 1 mol sample of liquid water at standard temperature and pressure conditions. When electric current is applied through the sample, the reaction



takes place. Using the data above, we may calculate the energy required to drive the reaction.

Rummaging through the various energy quantities studied previously, observe that the enthalpy  $H = U + PV$  matches the scenario. From thermochemistry data, we find that the enthalpy decreases by  $\Delta H = -286$  kJ. (Note: of the 286 kJ

that enters the system, an amount of work equal to  $1\text{atm} \times \Delta V = 4\text{kJ}$  is spent on shoving aside the atmosphere to make room for the new gases, with 282 kJ remaining.)

The entropy of the reaction is

$$\begin{aligned}\Delta S &= S_{H_2 + \frac{1}{2}O_2} - S_{H_2O} \\ &= \left(131 + \frac{205}{2} - 70\right) \text{J K}^{-1} \\ &= 163 \text{J K}^{-1},\end{aligned}$$

thus the environment contributes (positive) energy

$$T\Delta S = (298 \text{K})(163 \text{J K}^{-1}) = 49 \text{kJ}.$$

Finally, the change in Gibbs free energy  $G = H - TS$  works out as  $\Delta G = \Delta H - T\Delta S = -286\text{kJ} + 49\text{kJ} = -237\text{kJ}$ , which ‘predicts’ the top-right value in the thermochemistry table. Evidently, the device driving electrolysis must only provide 237kJ per mole of water.

## 6.2 Entropy of Mixing

Consider two systems such gases, equally-dense liquids, certain solids, or any other *ideal mixtures*  $A$  and  $B$  that are in thermal contact but in diffusive isolation by a partition. When the partition is removed, the change in entropy is strictly due to mixing, thus the analysis is highly analogous to ideal gas expansion. For each system respectively, start from Equation (1.44) to write

$$\begin{aligned}\Delta S_A &= N_A K \ln \left(1 + \frac{V_B}{V_A}\right) \\ \Delta S_B &= N_B K \ln \left(1 + \frac{V_A}{V_B}\right),\end{aligned}$$

and let  $y$  equal the volume and number ratio of species  $B$  to species  $A$ .

The sum  $\Delta S_A + \Delta S_B$  is the *entropy of mixing* formula:

$$\Delta S_{mix} = N_A K [(1-y) \ln(1-y) - y \ln y] \quad (1.67)$$

Letting  $\chi_\alpha$  equal the ratio the volume and number ratio of either species over the total, the above formula is equivalent to:

$$\Delta S_{mix} = -(N_A + N_B) K (\chi_A \ln \chi_A + \chi_B \ln \chi_B) \quad (1.68)$$

### Problem 53

Show that the entropy of mixing for two equal portions  $N = N_A = N_B$  of ideal gas resolves to

$$\Delta S = 2NK \ln 2.$$

## Free Energy of a Mixture

Consider (the same) two systems (gases, equally-dense liquids, certain solids)  $A$  and  $B$  that are in thermal contact but in diffusive isolation by a partition. Before the partition is removed, the Gibbs free energy is

$$G = \mu_A N_A + \mu_B N_B,$$

where letting  $N = N_A + N_B$  and  $x = N_B/N$ , we have

$$G = \mu_A N (1-x) + \mu_B N x = (1-x) G_A^0 + x G_B^0,$$

where  $G_A^0 = \mu_A N$  and  $G_B^0 = \mu_B N$  denote the unmixed energies. When the partition is removed, the total Gibbs free energy is simply

$$G_{mix} = (1-x) G_A^0 + x G_B^0 + T\Delta S_{mix}. \quad (1.69)$$

## 6.3 Dilute Solutions

Consider a system that initially consists of  $N_A$  particles of species  $A$ . According to Equation (1.58), the Gibbs free energy reads

$$G = N_A \mu_0(T, P)$$

at fixed temperature and pressure. The volume of the system may be considered as the sum of  $N_A$  volume elements.

A single particle of species  $B$  added to the system will ‘freely expand’ (isothermally) into the existing volume in analogy to Equation (1.44), contributing  $-KT \ln(N_A)$  to the Gibbs free energy. The chemical binding energy is represented by some unknown function  $f(T, P)$ , so we write the energy change as

$$dG = f(T, P) - KT \ln(N_A).$$

Adding a second particle of species  $B$  is not a matter of taking  $dG \rightarrow 2dG$  due to the indistinguishability of particles. It follows that for two particles of species  $B$ , the total correction to the Gibbs free energy is

$$dG = 2f(T, P) - 2KT \ln N_A + KT \ln 2.$$

Generalizing to  $N_B$  particles while maintaining the dilute limit  $N_B \ll N_A$  particles is straightforward. The  $KT \ln 2$  term generalizes to  $KT \ln(N_B!)$ , which by Stirling’s approximation becomes  $KT(N_B \ln N_B - N_B)$ . Finally, we have the Gibbs free energy of a dilute solution,

$$\begin{aligned}G &= N_A \mu_0(T, P) + N_B f(T, P) - N_B KT \ln N_A \\ &\quad + N_B KT \ln N_B - N_B KT.\end{aligned} \quad (1.70)$$

The chemical potentials of species  $A$  and  $B$  are readily calculated from the Gibbs free energy. These are:

$$\begin{aligned}\mu_A &= \left( \frac{\partial G}{\partial N_A} \right)_{T,P,N_A} \\ &= \mu_0(T, P) - \frac{N_B K T}{N_A}\end{aligned}\quad (1.71)$$

$$\begin{aligned}\mu_B &= \left( \frac{\partial G}{\partial N_B} \right)_{T,P,N_B} \\ &= f(T, P) + K T \ln \left( \frac{N_B}{N_A} \right)\end{aligned}\quad (1.72)$$

## 6.4 Osmotic Pressure

Consider a system of total volume  $V$  and number of particles solvent  $N_A$ . Next, divide the system with a semipermeable membrane and introduce some number of solute particles  $N_B$  on one side of the membrane. The membrane is tuned to allow the passage of solute particles, but not solvent particles. It follows that the pressure is weakly discontinuous across the membrane, and so too is the chemical potential on either side of the membrane, leading us to write

$$\mu_0(T, P_2) \approx \mu_0(T, P_1) + (P_2 - P_1) \frac{\partial \mu_0}{\partial P}.$$

Using Equation (1.71) for the chemical potential of the solvent particles, arrive at

$$(P_2 - P_1) \frac{\partial \mu_0}{\partial P} = \frac{N_B K T}{N_A}.$$

Of course, the derivative  $\partial \mu_0 / \partial P$  is simply  $V / N_A$  at constant  $T$  and  $N$ , and we arrive at

$$(P_2 - P_1) = \frac{N_B K T}{V}, \quad (1.73)$$

a result known as the *van't Hoff* formula. The pressure difference  $P_2 - P_1$  is known as the *osmotic pressure*.

## 6.5 Fugacity

As a dilute solution tends to equilibrium, the pressure required for the system to become diffuse and behave like ideal gas is called the *fugacity*. Begin by considering the entropy of freely-expanding ideal gas

$$S = N K \ln \left( \frac{V_f}{V_i} \right),$$

which also obeys  $P_i V_i = P_f V_f$ . Next, insert  $S$  into the definition (1.49) of chemical potential to get

$$\mu = \mu_0 + K T \ln \left( \frac{P_f}{P_i} \right),$$

where the  $\mu_0$  term has been imposed into the equation to handle dilute solutions. The ideal gas has  $\mu_0 = 0$ .

The above result generalizes to multiple dilute solutions. Let the ‘initial’ pressure  $P_i$  equal the sum  $P$  of all partial pressures, so drop the subscript. The  $j$ -th partial substance thus obeys

$$\mu_j = \mu_0 + K T \ln \left( \frac{P_j}{P} \right), \quad (1.74)$$

which generalizes again to non-ideal gases by introducing a van der Waals constant  $b$  as

$$\mu_j = \mu_0 + K T \ln \left( \frac{P_j}{P} \right) + b P,$$

which is equivalent to adding a dimensionless term  $\phi$  into the ln-term of Equation (1.74). Note that we have deployed a simplified van der Waals equation  $P(V - Nb) = NKT$ .

### Problem 54

Show that:

$$bP = K T \ln \phi$$

The dimensionless quantity  $\phi$  is called the *fugacity coefficient*, and the bare term ‘fugacity’ typically refers to the modified pressure

$$f = \phi P. \quad (1.75)$$

Fugacity comes into play when describing non-ideal gases near the ideal gas limit. Paraphrasing the differential version of Equation (1.74) for one chemical species, we define a formula that *replaces* pressure with fugacity:

$$d\mu = K T d(\ln f) \quad (1.76)$$

Immediately following definition (1.76), we solve for  $f$  to write

$$f = \exp \left( \frac{\mu - \mu_0}{K T} \right).$$

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