5.1 Processes of Heat Transfer

There are three ways that a substance can transfer energy to its environment or two another substance:

- Radiation: transfer of heat through the emission of electromagnetic waves.
- Convection: transfer of heat through bulk motion of liquid or gas
- Conduction: transfer of heat by contact

5.2 Compression Work

The most common (therefore important) type of work we can do on a gas is to compress it. Consider a gas of n moles in a cylinder of volume V with cross-sectional area A. A force can be applied to a piston which will compress the gas. Eq. 1.25 in the text should read

$$dW = \mathbf{F} \bullet \mathbf{dr} \tag{38}$$

This is the amount of work done by the external forcing agent when the force $\mathbf{F}$ is applied to the piston through a distance $\mathbf{dr}$. We want to invoke the IGL here, but if the piston is pushed to quickly, the pressure in the gas is undefined (pressure will be higher near the piston as the gas piles up near the rapidly moving piston during compression). So, we imagine compressing the gas quasistatically. In quasi-static compression, the piston is moved slowly such that the gas is always in equilibrium and the pressure is uniform and well-defined. This amounts to ensuring that you push the piston at a speed less than the speed of sound in the gas.

Using $F = PA$ in Eq. 1.25 in the text (Eq. 38 above) give

$$dW = -PAdr.$$

The (-) sign comes from our convention that the work must be positive when an external agent (the pushing force) acts *on* the gas. Since $dr < 0$ for compression due to the applied force, the (-) sign in $dW = -PAdr$ ensures that our convention is upheld. Notice that $Adr = dV$. Integrating gives

$$W = -\int PdV \tag{39}$$

This is an important relation that we will return to often. Eq. 39 is our starting point for all compression work problems.

There are several interesting cases to consider in the application of Eq. 39.

- Isobaric Compression and Expansion:

  If somehow, the pressure in the gas were constant (isobaric) during compression or expansion, we would have:

  $$W_{\text{isobaric}} = -P\Delta V. \tag{40}$$

  Draw an isobaric expansion of a gas from V_1 to V_2 on a PV diagram.

- Isochoric Compression and Expansion:

  Isochoric refers to processes in which the volume does not change. Clearly, in this case, the work done is zero (like the work done by someone pushing against an immobile wall).

  $$W_{\text{isochoric}} = 0 \tag{41}$$

  Draw an isochoric expansion of a gas from V_1 to V_2 on a PV diagram.

- Isothermal Compression and Expansion:

  Here the temperature is held constant by allowing heat to leave the cylinder during compression and allowing heat to enter the cylinder during expansion. If the gas is described by the IGL, then we can rewrite the pressure as $P = NkT/V$. Substituting this into Eq. 39, we have $W = -NkT\int dV/V$ where T is outside the integral because we have assumed an isothermal (constant temperature) process. So, the work done in compressing or expanding a gas from V_1 to V_2 at constant temperature is

  $$W_{\text{isothermal}} = -NkT\ln\left(\frac{V_2}{V_1}\right). \tag{42}$$

  Draw an isothermal expansion of a gas from V_1 to V_2 on a PV diagram.

- Adiabatic Compression and Expansion

  Adiabatic refers to a process in which no heat enters or leaves the system. In practice this might mean that the compression or expansion occurs quickly enough so that heat does not have the time to escape or enter the cylinder (yet still slowly enough to satisfy our quasi-static constraint). Referring to the First Law of Thermodynamics (the one that defines thermal energy), $\Delta U = Q + W$, we see that an adiabatic process will be one in which the change in internal energy of the gas is entirely due to the work done on the gas: $W_{\text{adiabatic}} = \Delta U$

  The change in internal energy is entirely thermal (work cannot affect rest energies, bond energies, etc.), so

  $$W_{\text{adiabatic}} = \Delta U_{\text{thermal}} \tag{43}$$

  Draw an adiabatic expansion of a gas from V_1 to V_2 on a PV diagram.

A Simple Example of Computing Net Work Done in a Cycle of Expansion and Compression

Consider the cycle shown in the figure. (1) An ideal gas undergoes *isochoric* pressurization from P_1 to P_2 at the constant volume V_1; (2) *isobaric* expansion from V_1 to V_2 at pressure P_2; (3) *isochoric* de-pressurization from P_2 to P_1 at volume V_2; and (4) *isobaric* compression from V_2 to V_1. We would like to compute the work done in this cycle. We will do so by computing the work done along each of the paths (1-4).

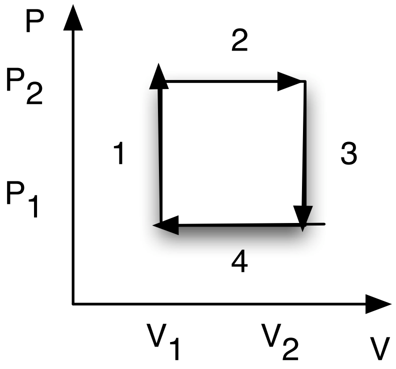

Figure 1: **default**

- Path 1: Here there is no change in volume, so the work done $W_1 = 0$.
- Path 2: Isobaric Expansion: $W_2 = -P_2\Delta V = -P_2(V_2 - V_1) < 0$. The gas has done work on the environment in pushing against the piston ($W < 0$).
- Path 3: No change in volume, so the work $W_3 = 0$.
- Path 4: Isobaric Compression: $W_4 = -P_1\Delta V = -P_1(V_1 - V_2) > 0$. The gas has been compressed by the piston, so the external agent has done work on the gas ($W > 0$).

The net work done by (on?) the gas is then $W_1 + W_2 + W_3 + W_4$. Summing the above contributions, we find

$$W_{\text{net}} = -P_2(V_2 - V_1) + -P_1(V_1 - V_2) = (P_1 - P_2) \times (V_2 - V_1) < 0 \tag{44}$$

The total work done is negative meaning, according to our convention, that the gas has performed work on the environment. This is the basis of all heat engines (e.g., internal combustion engine).

An important Observation:

Compare the area enclosed in the cycle with the net work that we've just calculated. This is a general result for PV cycles!

Now Compute the Change in Internal Energy of the Gas in this Cycle

The total Thermal energy at any point in the cycle depends only on the temperature: $U_{\text{thermal}} = \frac{f}{2}NkT$. The temperature at each point can be obtained from the ideal gas law $PV = NkT$. It is a worthwhile exercise to compute the change in internal energy along each leg of the cycle. You will find a general result for all closed cycles on a PV diagram:

$$\Delta U_{\text{thermal}} = 0 \text{ around any closed cycle on the PV diagram} \tag{45}$$

Finally, what is the net heat added (removed?) from the gas? Hint: First Law of Thermo!

We will return to engine cycles in a subsequent chapter.

5.3 The Adiabatic Exponent

The text (p.25-26) derives some useful relations for adiabatic processes in an ideal gas. You can check the text for the derivation, but you should be aware of these important adiabatic relations:

$$VT^{f/2} = \text{constant} \tag{46}$$

and

$$V^{\gamma}P = \text{constant, where } \gamma \equiv \frac{f+2}{f} \tag{47}$$

γ is called the *adiabatic exponent.*

Example: Consider the adiabatic expansion of an ideal gas from V_1 to $V_2 = 2V_1$. In case (a), we take the gas to be monatomic ($f = 3$). In case (b), we take the gas to be diatomic with rotational modes available ($f = 5$). Which case will result in the greatest drop in pressure if both gases start at the same pressure P_1?

From the above adiabatic relations, we that $P_2/P_1 = (V_1/V_2)^{\gamma}$. We know that $V_1/V_2 = 1/2$, and so we find that for case (a), $P_2/P_1 = 0.315$, while, for case (b), we have $P_2/P_1 = 0.379$. The monatomic gas will experience a greater pressure drop than the diatomic gas. Does this make sense? Can you see why this must be true?

5.4 Getting Started on Problem 1.40

We know that temperature through the troposphere (bottom-most 10-15 km of atmosphere) decreases linearly with altitude z. If the temperature gradient $|dT/dz|$ in this region exceeds a certain critical value, then a rising mass of air will experience convection: the surrounding atmosphere is cooling faster than the rising air mass so the air mass remains warmer at all times than the surrounding atmosphere. Problem 1.40(a) asks you to consider the *adiabatic* expansion of an air mass as it rises. Picture a slab of air (like we did in problem 1.16) that is subject to the IGL. The pressure in the air parcel is $P = nRT/V$. For adiabatic expansion, we have

$$VT^{f/2} = \text{constant} \rightarrow \frac{1}{V} = \frac{T^{f/2}}{\text{constant}}. \tag{48}$$

So, the pressure in the air parcel is given by

$$P = \frac{nRT^{(f+2)/2}}{\text{constant}}$$

This is an equation of state for the air parcel as it adiabatically expands. We can easily find the desired relation for dT/dP by first computing dP/dT and recognizing that T and P are well behaved functions so its ok to invert dP/dT to get dT/dP. The result is

$$\frac{dT}{dP} = \frac{2}{f+2}\frac{T}{P} \tag{49}$$

6 Heat Capacities and Specific Heats

The heat capacity of a substance is the amount of heat that you need to give the substance to raise its temperature through a given ΔT. Clearly you need to add more heat to an ocean to raise its temperature by 5 °C than you need to add to a cup of saltwater to raise its temperature by the same amount. Therefore heat capacity (C) depends on the amount of the substance in question, and is less of a useful measure than the related concept of *specific heat.*

The specific heat (c) of a substance is the heat capacity per unit mass. In terms of the specific heat, the amount of heat Q needed to raise the temperature by ΔT of a mass m of a substance with specific heat c is:

$$Q = mc\Delta T \tag{50}$$

Your text points out that this is an ambiguous definition: from the 1st Law, we know that $Q = \Delta U - W$. Therefore, we expect that the specific heat is given by $c = (\Delta U - W)/m\Delta T$. So, specific heat can be affected by

- the internal energy U which in turn, depends on f (the number of quadratic degrees of freedom enjoyed by the molecule),
- the work W done on or by the gas.

To remove the ambiguity, we recognize two cases:

constant volume heat capacity

In the first case, we consider processes in which the volume of the substance is held constant. In this case, the work done on/by the substance is zero since $W = -\int PdV$. The heat capacity in this case is called the "heat capacity at constant volume and is abbreviated C_V. Likewise, the specific heat at constant volume is abbreviated c_V. Since $W = 0$, we must have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{51}$$

where the V subscript on the partial derivative means that the derivative is evaluated for fixed volume. As an example, the specific heat at constant volume for liquid water is 4.2 J/gram-°C. It takes 4.2 joules or 1 calorie to raise the temperature of 1 gram of liquid water by one degree Celsius.

constant pressure heat capacity Often, things expand when heated, so that work is done on the environment by the substance during expansion ($W < 0$ and $C > C_V$). In such a case, the constant volume specific heat or heat capacity is not a useful measure. Instead, we consider the other case that can be easily calculated - constant pressure. If P is held fixed, the work done $W = -\int PdV$ is simply $-P\Delta V$. So, the heat capacity at constant pressure is

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P$$

Taking the appropriate limit, we have the final expression for the heat capacity at constant pressure

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{52}$$

The second term above is the heat needed to compensate for energy lost through work done on the environment. This is usually small as we will see.

heat capacities of solids and gasses

We know that for "classical solids and gasses" (ignoring quantum effects at very low temperatures), the internal energy U is just

$$U = \frac{1}{2}NfkT.$$

Therefore, $C_V = (1/2)Nfk$ is (a) a constant, and (b) a useful way to measure f and thereby learn something about the type of molecule comprising the gas or solid.

- Monatomic Gas:

$$f = 3 \Rightarrow C_V = \frac{3}{2}Nk = \frac{3}{2}nR \tag{53}$$

- Diatomic Gas (room temperature so rotations are present, but no vibrations):

$$f = 5 \Rightarrow C_V = \frac{5}{2}Nk = \frac{5}{2}nR \tag{54}$$

- Solid:

$$f = 6 \Rightarrow C_V = 3Nk = 3nR \tag{55}$$

  The last example above (that the heat capacity of a solid is just $3nR$ is a famous experimental result known as the *Dulong-Petit Heat Capacity.*

6.1 Relationship between C_P and C_V

For an ideal gas,

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V$$

Why? Because U only depends on T. Therefore,

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

which can be simplified using the IGL expression $V = nRT/P$:

$$C_P = C_V + nR \tag{56}$$

This is a nice, simple result that we would not have guessed at - the difference between the constant pressure heat capacity and the constant volume heat capacity for an ideal gas is proportional to the number of moles of gas present.

6.2 A simple example application

This is really more of a PHYS 203 problem, so you should have seen this before: Consider a mass $m_1 = 200$ g of coffee at temperature $T_1 = 90°C$ in an insulated (styrofoam or the like) cup. Now add a mass $m_2 = 10$ g of cream at a temperature of $T_2 = 20°C$. Since coffee and cream are both mostly water their specific heats are the same as water. What is the final temperature T_F of the mixture of cream and coffee?

Since the cup is insulated, there is no heat exchanged with the outside world. $\Delta Q = \Delta Q_{\text{coffee}} + \Delta Q_{\text{cream}} = 0$:

$$\begin{aligned} 0 &= \Delta Q_{\text{coffee}} + \Delta Q_{\text{cream}} \\ &= m_1 c \Delta T_1 + m_2 c \Delta T_2 \\ &= m_1 c (T_F - T_1) + m_2 c (T_F - T_2) \end{aligned}$$

Solving for T_F, we find

$$T_F = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2} = \frac{(200)(90) + (10)(20)}{210} = 86.7°C$$

7 Latent Heats of Transformation

This is the subject of *phase transformations* - the change in state from one phase to another such as the transformation from a solid to a liquid, liquid to a vapor, or from an insulator to a superconductor.

In the first couple examples above (melting and evaporation), there is a *latent heat* associated with the phase transformation. Latent means ”hidden” in the following sense. As water ice is warmed it absorbs heat from its environment. Its temperature increases according to $Q = mc_{ice}\Delta T$. The effect of this heat is not hidden - it is manifest in the temperature increase. However, something funny happens when the ice warms to a temperature of $0°C$. Additional heat added to the ice does not result in an increase in the temperature of the ice. This heat is ”hidden” or latent. Instead, the latent heat goes into breaking molecular bonds that hold the water molecules together in the ice lattice. **A phase transition is characterized by a latent heat required to change the state of the substance while the temperature remains constant.**

Latent Heats:

Process	$L(J/kg)$
Ice melting	3.3×10^5
Water Vaporizing	2.26×10^6

7.1 Vaporization of Water

How much energy is needed to vaporize a cup (200 grams) of water at room temperature? There are two processes here: (1) raising the temperature from T_0 to T_v requires an amount of heat $Q_1 = mc\Delta T$; (2) vaporizing the water at T_v requires an amount of heat $Q_2 = mL_v$.

- Raising the temperature to the boiling point:

$$Q_1 = mc\Delta T = (0.2\text{ kg})(4186\text{J/kg}^{\circ}C)(100°C - 20°C) = 6.7 \times 10^4\text{ J} \tag{57}$$

- Vaporizing the water at T_v:

$$Q_2 = mL_v = (0.2\text{ kg})(2.26 \times 10^6\text{J/kg}) = 4.52 \times 10^5\text{ J} \tag{58}$$

The total energy needed is then $Q_1 + Q_2 = 5.19 \times 10^5$ J.

If a 600W microwave oven could dump all of its energy into the cup of water (100% efficiency), how long would it take to vaporize the water in the cup?

$$\Delta t = \frac{Q}{P} = \frac{5.19 \times 10^5\text{ J}}{600\text{ J/s}} = 8.65 \times 10^2\text{ sec.} \approx 14\text{ minutes} \tag{59}$$

7.2 Snow Melting Example

In December, solar intensity (during the day) is about $80W/m^2$ in Chicago. Let us say that the ground is covered by a layer of snow 5 cm deep. The snow is 50% air and 50% water. How long will it take this snow layer to melt assuming the air and surface temperature is near $0°C$? Snow is known to reflect about 90% of the incident energy from the sun, so only 10% of the solar insolation can go into the heat of fusion.

Consider a patch of snow $1m^2$ in area and 5 cm deep. The volume of this patch is 0.05 m^3. The volume of ice contained in the patch is 0.025 m^3. The mass of ice is thus $m = \rho_{ice}V_{ice} = (1000kg/m^3)(0.025m^3) = 25kg$.

The heat required to melt the ice is:

$$Q = mL_f = (25\text{ kg})(3.3 \times 10^6\text{ J/kg}) = 8.3 \times 10^6\text{ J} \tag{60}$$

Let us assume that the sun shines for about 8 hours per day in December, in Chicago. The average solar power delivered to the snow patch is then

$$P = \frac{8}{24}80\text{ W} = 26.6\text{ W}$$

The time required to completely melt the snow is

$$\Delta t = \frac{Q}{P} = \frac{8.3 \times 10^6\text{ J}}{26.6\text{ W}} = 3.12 \times 10^5\text{ seconds} = 3.6\text{ days}$$

Does this make sense in terms of your memory of snow disappearing from the ground even though both the surface and air are colder than 0 °C? What other processes have been neglected in this analysis? Will these processes contribute significantly to the time?

7.3 Physics of Endurance Athletes

When we come back to classical thermodynamics in chapter 5 to learn about thermodynamic efficiencies, we'll be able to really tackle problems like the following with more rigor. For now, we know just enough to be dangerous. So, let's see what we can say about the thermodynamics of running.

In order to run (or swim or bike...) your body must convert fat and glycogen into energy. As we will see in chapter 5, this conversion is very inefficient. Only about 10-12% of the food energy is transformed into mechanical energy. The remainder is dissipated as heat. The blood carries the heat to the skin to dissipate it through evaporation and perspiration. On the surface, this seems terribly inefficient. However, all heat engines are limited to a maximum theoretical efficiency and the body is no different. Yet, the body could in principle be more efficient - converting more of the available energy to mechanical work. Instead, the body does some very clever things with the waste heat, without which endurance sports of most kinds would not be possible.

We know from a previous class that the body radiates energy according to the Stefan Boltzmann radiation law $P = e\sigma AT^4$ given a core body temperature of 98.6°F and a typical surface area A for an adult, this radiated power is on the order of 100 W. This is your resting metabolism (basal metabolic rate) - the rate at which your body loses energy through radiation when it does nothing but sit and maintain respiration and basic brain activity. When you do thermodynamics homework, your radiated output is actually measurably higher than this base rate because of the extra clock cycles used by your brain. Implication: You can lose weight by thinking alone! But don't think alone. Find a thinking partner to spot you.

Consider a 150 lb distance runner burning glycogen and fat according to the table below for a 7.5 mph pace. The hydrogen atoms in the fat molecule are transferred to oxygen to form water. The runner consumes energy at a rate of 423 Cal per 30 minutes or about 984 Watts (do this conversion yourself). Where does this energy go? As we've discussed only about 10-12% of the available energy goes into mechanical motion (overcoming air resistance to maintain a constant speed). 10% of 984 W is 98.4W. The remainder - 886 W is used to heat and evaporate water through perspiration on the skin. At what rate is the water evaporated? This is the rate at which the athlete must take in water during the run. The evaporation rate depends on a variety of environmental conditions such as air temperature, humidity, wind speed, etc. However, we can make some back-of-the-envelope estimates to get a ball-park figure for the evaporation rate using the basic thermodynamics we've developed. There are two processes:

- the water is heated from its initial temperature to the final temperature of the body. Assume that the water is initially at room temperature: $\Delta T = 37 - 21°C = 16°C$. The required energy to accomplish this is:
$$Q_1 = mc\Delta T$$
- the heated water is evaporated:
$$Q_2 = mL_v$$
The total heat require is $Q_1 + Q_2 = m(c\Delta T + L_v)$. The latent heat of evaporation at $T = 37°C$ is $L_v = 2.42 \times 10^6 J/kg$.

Setting $Q_1 + Q_2$ equal to the 984 J, we can solve for the mass of water that is evaporated per second:

$$m = \frac{Q_1 + Q_2}{c\Delta T + L_v)} = \frac{984 J/s}{(4186 J/kg)(16°C) + 2.42 \times 10^6 J/kg} = 4 \times 10^{-4} kg/s$$

So, in one hour, this runner loses 1.4 kg of water to evaporation - around 1.4 liters or 47 fluid ounces! Note that most of the energy goes toward the evaporation process. The heating from room temperature to body temperature requires a comparatively tiny fraction of the energy used.

As anyone who has run in the heat of the summer knows, high ambient temperatures and humidity can seriously interfere with your ability to remove excess heat through perspiration. Recall that conduction transport is proportional to the temperature difference between the body and the environment. As the ambient temperature approaches 37 $°C$, the conduction rate goes to zero. As the humidity of the air increases, the partial pressure of water increases which inhibits evaporation of water from the skin - the skin and air approach an evaporative equilibrium where just as much water is condensed onto the skin as evaporates from the skin. The net effect of these inhibitory processes is that the body retains the excess heat generated and the internal body temperature rises. Humans have an exceedingly narrow range of survivable core temperatures, so such an increase due to the 984 W of excess power now dumped into the body can quickly result in serious injury or death, particularly to children for whom the lower ratio of skin surface to body weight results in less efficient cooling in general.

Modeling that 150 lb runner as a bag of liquid water at a temperature of 37 $°C$ calculate the time it takes to raise the temperature of the body by 1 $°C$ due to a $Q/t = 984W$.

$$\frac{mc\Delta T}{\Delta t} = 984 J/sec \Rightarrow \Delta t = \frac{mc\Delta T}{984W} = \frac{(75kg)(4186 J/kg°C)(1°C)}{984 J/s} = 319 sec \approx 5.3 \text{ minutes.}$$

Moral of the story: Athletes in endurance sports can quickly get into trouble with overheating or under hydration.

Energy Demands of Physical Activities

Activity	**Calories/ lb./min.**	**Calories burned during 30 minutes of activity at various body weights**				
		110 lb.	***125 lb.***	***150 lb.***	***175 lb.***	***200 lb.***
Aerobic dance (vigorous)	0.062	204	234	279	327	372
Basketball (vigorous/full crt.)	0.097	321	363	438	510	582
Bicycling						
13 mph	0.045	150	168	204	237	270
19 mph	0.076	252	285	342	399	456
25 mph	0.139	459	522	627	729	834
Golf (carrying clubs)	0.045	150	168	204	237	270
Rowing (vigorous)	0.097	321	363	438	510	582
Running						
5 mph	0.061	201	228	276	321	366
7.5 mph	0.094	309	354	423	492	564
10 mph	0.114	375	429	513	600	687
Studying	0.011	36	42	51	57	66
Swimming						
20 yd./min.	0.032	105	120	144	168	192
45 yd./min.	0.058	192	219	261	306	348
50 yr./min.	0.070	231	264	315	369	420
Tennis (beginner)	0.032	105	120	144	168	192
Walking (briskly)						
3.5 mph	0.035	117	132	156	183	210
4.5 mph	0.048	159	180	216	252	288
Weight Lifting						
Light-Moderate	0.023	76	86	104	121	138
vigorous	0.045	149	169	203	236	270