

## CHAPTER 8

### HEAT CAPACITY, AND THE EXPANSION OF GASES

#### 8.1 Heat Capacity

**Definition:** The *heat capacity* of a body is the quantity of heat required to raise its temperature by one degree. Its SI unit is  $\text{J K}^{-1}$ .

**Definition:** The *specific heat capacity* of a substance is the quantity of heat required to raise the temperature of unit mass of it by one degree. Its SI unit is  $\text{J kg}^{-1} \text{K}^{-1}$ .

**Definition:** The *molar heat capacity* of a substance is the quantity of heat required to raise the temperature of a molar amount of it by one degree. (I say "molar amount". In CGS calculations we use the mole – about  $6 \times 10^{23}$  molecules. In SI calculations we use the kilomole – about  $6 \times 10^{26}$  molecules.) Its SI unit is  $\text{J kilomole}^{-1} \text{K}^{-1}$ .

Some numerical values of specific and molar heat capacity are given in Section 8.7.

One sometimes hears the expression "the specific heat" of a substance. One presumes that what is meant is the specific heat capacity.

The above definitions at first glance seem easy to understand – but we need to be careful. Let us imagine again a gas held in a cylinder by a movable piston. I choose a gas because its volume can change very obviously on application of pressure or by changing the temperature. The volume of a solid or a liquid will also change, but only by a small and less obvious amount. If you supply heat to a gas that is *allowed to expand at constant pressure*, some of the heat that you supply goes to doing external work, and only a part of it goes towards raising the temperature of the gas. On the other hand, *if you keep the volume of the gas constant*, all of the heat you supply goes towards raising the temperature. Consequently, more heat is required to raise the temperature of the gas by one degree if the gas is allowed to expand at constant pressure than if the gas is held at constant volume and not allowed to expand. Thus the heat capacity of a gas (or any substance for that matter) is greater if the heat is supplied at constant pressure than if it is supplied at constant volume. Thus we have to distinguish between the *heat capacity at constant volume*  $C_V$  and the *heat capacity at constant pressure*  $C_P$ , and, as we have seen  $C_P > C_V$ .

If the heat is added at constant volume, we have simply that  $dU = dQ = C_V dT$ .

One other detail that requires some care is this. The specific heat capacity of a substance may well vary with temperature, even, in principle, over the temperature range of one degree mentioned in our definitions. Therefore, we really have to define the heat capacity at a given temperature in terms of the heat required to raise the temperature by an infinitesimal amount rather than through a finite range. Thus it is perhaps easiest to **define** heat capacity at constant volume in symbols as follows:

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$$C_V = \left( \frac{\partial U}{\partial T} \right)_V. \quad 8.1.1$$

(Warning: Do not assume that  $C_p = (\partial U / \partial T)_p$ . That isn't so. The correct expression is given as equation 9.1.13 in Chapter 9 on Enthalpy.)

As with many equations, this applies equally whether we are dealing with total, specific or molar heat capacity or internal energy.

If heat is supplied at constant pressure, some of the heat supplied goes into doing external work  $PdV$ , and therefore

$$C_p dT = C_V dT + P dV. \quad 8.1.2$$

For a mole of an *ideal gas* at *constant pressure*,  $P dV = R dT$ , and therefore, for an ideal gas,

$$C_p = C_V + R, \quad 8.1.3$$

where, in this equation,  $C_p$  and  $C_V$  are the *molar* heat capacities of an ideal gas.

We shall see in Chapter 10, Section 10.4, if we can develop a more general expression for the difference in the heat capacities of *any* substance, not just an ideal gas. But let us continue, for the time being with an ideal gas.

In an ideal gas, there are no forces between the molecules, and hence no potential energy terms involving the intermolecular distances in the calculation of the internal energy. In other words, the internal energy is independent of the distances between molecules, and hence the internal energy is independent of the volume of a fixed mass of gas if the temperature (hence kinetic energy) is kept constant. That is, for an ideal gas,

$$\left( \frac{\partial U}{\partial V} \right)_T = 0. \quad 8.1.4$$

Let us think now of a *monatomic* gas, such as helium or argon. When we supply heat **to** (and raise the temperature of) an ideal monatomic gas, we are increasing the translational kinetic energy of the molecules. If the gas is *ideal*, so that there are no intermolecular forces then *all* of the introduced heat goes into increasing the translational kinetic energy (i.e. the temperature) of the gas. (Recall that a gas at low pressure is nearly ideal, because then the molecules are so far apart that any intermolecular forces are negligible.) Recall from Section 6.5 that the translational kinetic energy of the molecules in a mole of gas is  $\frac{3}{2}RT$ . The molar internal energy, then, of an ideal monatomic gas is

$$U = \frac{3}{2}RT + \text{constant}. \quad 8.1.5$$

From equation 8.1.1, therefore, the molar heat capacity at constant volume of an ideal monatomic gas is

$$C_V = \frac{3}{2}R. \quad 8.1.6$$

The molar heat capacities of real monatomic gases when well above their critical temperatures are indeed found to be close to this.

When we are dealing with *polyatomic* gases, however, the heat capacities are greater. This is because, when we supply heat, only some of it goes towards increasing the translational kinetic energy (temperature) of the gas. Some of the heat goes into increasing the *rotational* kinetic energy of the molecules. (Wait! Some of you are asking yourselves: "But do not atoms of helium and argon rotate? Do they not have rotational kinetic energy?" These are very good questions, but I am going to pretend for the moment that I haven't heard you. Perhaps, before I come to the end of this section, I may listen.)

When two molecules collide head on, there is an interchange of translational kinetic energy between them. But if they have a glancing collision, there is an exchange of translational and rotational kinetic energies. If millions of molecules are colliding with each other, there is a constant exchange of translational and rotational kinetic energies. When a dynamic equilibrium has been established, the kinetic energy will be shared equally between each degree of translational and rotational kinetic energy. (This is the *Principle of Equipartition of Energy*.) We know that the translational kinetic energy per mole is  $\frac{3}{2}RT$  - that is,  $\frac{1}{2}RT$  for each translational *degree of freedom* ( $\frac{1}{2}m\overline{u^2}$ ,  $\frac{1}{2}m\overline{v^2}$ ,  $\frac{1}{2}m\overline{w^2}$ ). There is an equal amount of kinetic energy of rotation (with an exception to be noted below), so that the internal energy associated with a mole of a polyatomic gas is  $3RT$  plus a constant, and consequently the molar heat capacity of an ideal *polyatomic* gas is

$$C_V = 3R. \quad 8.1.7$$

It takes twice the heat to raise the temperature of a mole of a polyatomic gas compared with a monatomic gas.

The exception we mentioned is for *linear* molecules. These are molecules in which all the atoms are in a straight line. This necessarily includes, of course, all diatomic molecules (the oxygen and nitrogen in the air that we breathe) as well as some heavier molecules such as  $\text{CO}_2$ , in which all the molecules (at least in the ground state) are in a straight line. (The molecule  $\text{H}_2\text{O}$  is *not* linear.) In linear molecules, the moment of inertia about the internuclear axis is negligible, so there are only two degrees of rotational freedom, corresponding to rotation about two axes perpendicular to each other and to the internuclear axis. Thus there are five degrees of freedom in all (three of translation and two of rotation) and the kinetic energy associated with each degree of freedom is  $\frac{1}{2}RT$  per mole for a total of  $\frac{5}{2}RT$  per mole, so the molar heat capacity is

$$C_V = \frac{5}{2}R. \quad 8.1.8$$

*Summary:* A monatomic gas has three degrees of translational freedom and none of rotational freedom, and so we would expect its molar heat capacity to be  $\frac{3}{2}R$ .

A diatomic or linear polyatomic gas has three degrees of translational freedom and two of rotational freedom, and so we would expect its molar heat capacity to be  $\frac{5}{2}R$ .

A nonlinear polyatomic gas has three degrees of translational freedom and three of rotational freedom, and so we would expect its molar heat capacity to be  $3R$ .

How do real gases behave compared with these predictions? The monatomic gases (helium, neon, argon, etc) behave very well. The diatomic gases quite well, although at room temperature the molar heat capacities of some of them are a little higher than predicted, while at low temperatures the molar heat capacities drop below what is predicted. Indeed below about 60 K the molar heat capacity of hydrogen drops to about  $\frac{3}{2}R$  - just as if it had become a monatomic gas or, though still diatomic, the molecules were somehow prevented from rotating. The molar heat capacities of nonlinear polyatomic molecules tend to be rather higher than predicted.

First let us deal with why the molar heat capacities of polyatomic molecules and some diatomic molecules are a bit higher than predicted. This is because the molecules may *vibrate*. When we add heat, some of the heat is used up in increasing the rate of rotation of the molecules, and some is used up in causing them to vibrate, so it needs a lot of heat to cause a rise in temperature (translational kinetic energy). The possibility of vibration adds more degrees of freedom, and another  $\frac{1}{2}R$  to the molar heat capacity for each extra degree of vibration. To be strictly correct, the "number of degrees of freedom" in this connection is the number of squared terms that contribute to the internal energy. Each vibrational mode adds two such terms - a kinetic energy term and a potential energy term. This means that the predicted molar heat capacity for a nonrigid diatomic molecular gas would be  $\frac{7}{2}R$ . Polyatomic gases have many vibrational modes and consequently a higher molar heat capacity.

So - why is the molar heat capacity of molecular hydrogen not  $\frac{7}{2}R$  at all temperatures? Why is it about  $\frac{5}{2}R$  at room temperature, as if it were a rigid molecule that could not vibrate? True, at higher temperatures the molar heat capacity does increase, though it never quite reaches  $\frac{7}{2}R$  before the molecule dissociates. Why does the molar heat capacity decrease at lower temperatures, reaching  $\frac{3}{2}R$  at 60 K, as if it could no longer rotate?

Let us ask some further questions, which are related to these. We said earlier that a monatomic gas has no rotational degrees of freedom. Why not? True, the moment of inertia is very small, but, if we accept the principle of equipartition of energy, should not each rotational degree of freedom hold as much energy as each translational degree of freedom? Also, we said that a linear molecule has just two degrees of freedom. It is true that the moment of inertia about the internuclear axis is very small. This is not the same thing as saying that it cannot rotate about that axis. If all degrees of freedom equally share the internal energy, then the angular speed about the internuclear axis must be correspondingly large.

Now I could make various excuses about these problems. The fact is, however, that the classical model that I have described may look good at first, but, when we start asking these awkward questions, it becomes evident that the classical theory really fails to answer them satisfactorily. In truth, the failure of classical theory to explain the observed values of the molar heat capacities of

gases was one of the several failures of classical theory that helped to give rise to the birth of quantum theory. Quantum theory in fact accounts spectacularly well and in detail for the specific heat capacities of molecules and how the heat capacities vary with temperature. This topic is often dealt with on courses on statistical thermodynamics, and I just briefly mention the explanation here. The solution of Schrödinger's equation for a rigid rotator shows that the rotational energy can exist with a number of separated discrete values, and the population of these rotational energy levels is governed by Boltzmann's equation in just the same way as the population of the electronic energy levels in an atom. At temperatures of 60 K, the spacing of the rotational energy levels is large compared with  $kT$ , and so the rotational energy levels are unoccupied. Thus, in that very real sense, the hydrogen molecule does indeed stop rotating at low temperatures. The spacing of the energy level is inversely proportional to the moment of inertia, and the moment of inertia about the internuclear axis is so small that the energy of the first rotational energy level about this axis is larger than the dissociation energy of the molecule, so indeed the molecule cannot rotate about the internuclear axis. Vibrational energy is also quantised, but the spacing of the vibrational levels is much larger than the spacing of the rotational energy levels, so they are not excited at room temperatures. This has been only a brief account of why classical mechanics fails and quantum mechanics succeeds in correctly predicting the observed heat capacities of gases. It is a very interesting subject, and the reader may well want to learn more about it – but that will have to be elsewhere.

## 8.2 Ratio of the Heat Capacities of a Gas

The ratio of the heat capacities of a gas at constant pressure and at constant volume plays an important part in many calculations involving the expansion and contraction of gases. The ratio appears, for one example of many that could be chosen, in the theoretical expression for the speed of sound in a gas. The higher the ratio  $C_P/C_V$ , the faster the speed of sound. The ratio is generally given the symbol  $\gamma$ :

$$\frac{C_P}{C_V} = \gamma. \quad 8.2.1$$

Apart from any other reason, one reason for its importance is that the ratio is easier to measure precisely than either heat capacity separately. For example, you could determine it from a measurement of the speed of sound, which is easier than adding heat to a sample of gas at constant pressure and again at constant volume and measuring the rise in temperature.

We have seen that, for gases that behave as we would like them to behave, the molar heat capacities  $C_V$  at constant temperatures for monatomic, diatomic and nonlinear polyatomic gases without molecular vibration are respectively  $\frac{3}{2}R$ ,  $\frac{5}{2}R$  and  $3R$ . And since, for an ideal gas,  $C_P = C_V + R$ , (equation 8.1.3), we expect the corresponding values for  $C_P$  to be  $\frac{5}{2}R$ ,  $\frac{7}{2}R$  and  $4R$ . Thus the expected values of  $\gamma$  are  $5/3$ ,  $7/5$  and  $4/3$ .

### 8.3 Reversible Isothermal Expansion of an Ideal Gas

An ideal gas obeys the equation of state  $PV = RT$  ( $V$  = molar volume), so that, if a fixed mass of gas kept at constant temperature is compressed or allowed to expand, its pressure and volume will vary according to  $PV = \text{constant}$ . That is, Boyle's Law. We can calculate the *work done* by a mole of an ideal gas in a reversible isothermal expansion from volume  $V_1$  to volume  $V_2$  as follows.

$$W = \int_{V_1}^{V_2} P dV = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln(V_2/V_1). \quad 8.3.1$$

### 8.4 Reversible Adiabatic Expansion of an Ideal Gas

An adiabatic process is one in which no heat enters or leaves the system, and hence, for a reversible adiabatic process the first law takes the form  $dU = -P dV$ . But from equation 8.1.1,  $C_V = (\partial U / \partial T)_V$ . But the internal energy of an ideal gas depends only on the temperature and is independent of the volume (because there are no intermolecular forces), and so, for an ideal gas,  $C_V = dU / dT$ , and so we have  $dU = C_V dT$ . Thus for a reversible adiabatic process and an ideal gas,  $C_V dT = -P dV$ . (The minus sign shows that as  $V$  increases,  $T$  decreases, as expected.) But for a mole of an ideal gas,  $PV = RT = (C_p - C_V)T$ , or  $P = (C_p - C_V)T / V$ .

Therefore 
$$C_V dT = -(C_p - C_V)T dV / V. \quad 8.4.1$$

(You may be wondering whether  $C$  and  $V$  are molar, specific or total quantities. If you look at the equation you'll agree that it is valid whether the volume and heat capacities are molar, specific or total.)

Separate the variables and write  $\gamma$  for  $C_p/C_V$ :

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0. \quad 8.4.2$$

Integrate: 
$$TV^{\gamma-1} = \text{constant}. \quad 8.4.3$$

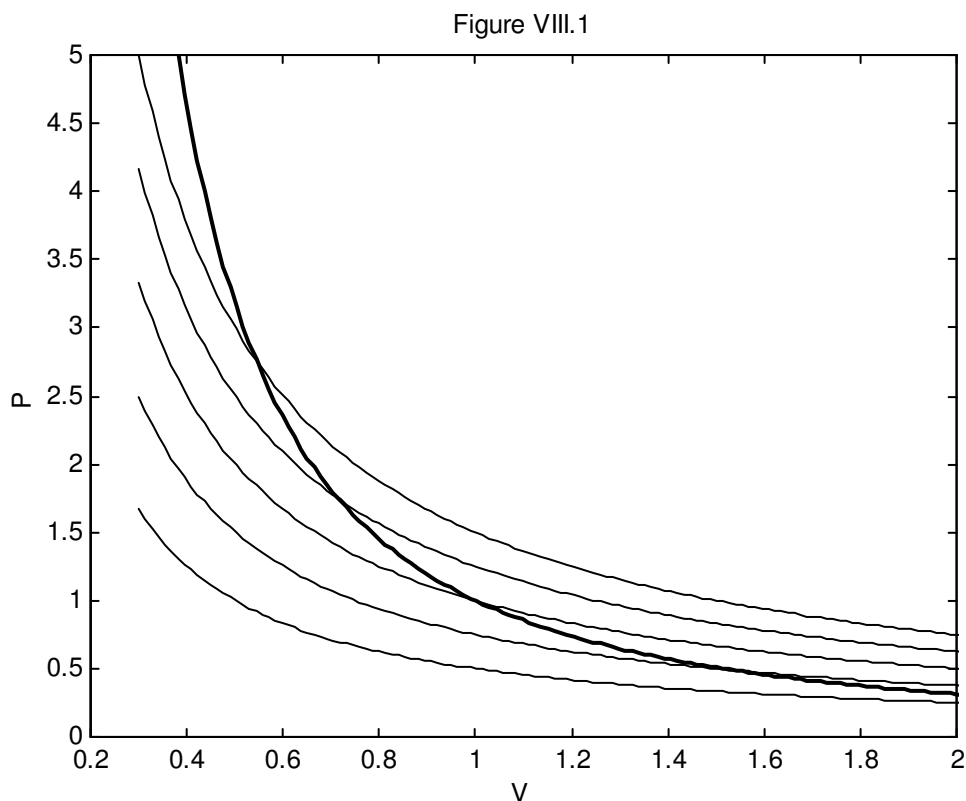
This shows how temperature and volume of an ideal gas vary during a reversible adiabatic expansion or compression. If the gas expands, the temperature goes down. If the gas is compressed, it becomes hot. Of course the pressure varies also, and the ideal gas conforms to the equation  $PV/T = \text{constant}$ . On elimination of  $T$  we obtain

$$PV^\gamma = \text{constant}. \quad 8.4.4$$

On elimination of  $V$  we obtain

$$P^{-(\gamma-1)}T^\gamma = \text{constant}. \quad 8.4.5$$

In figure VIII.1 I draw, as light curves, five isotherms – i.e. the paths that would be taken by an ideal gas in the  $PV$  plane in isothermal processes at five temperatures. I also show, as a heavier line, an *adiabat*,  $PV^\gamma = \text{constant}$ , which I calculated for  $\gamma = 5/3$ . The adiabat is steeper than the isotherms, and the curve shows that, as the gas expands adiabatically, the temperature drops. If you know the original temperature and the old and new volumes, equation 8.4.3 will enable you to calculate the new temperature. If you know the original temperature and the old and new pressures, equation 8.4.5 will enable you to calculate the new temperature. While these purely thermodynamic arguments show that a gas becomes hotter if you compress it, this is also to be expected at the microscopic level. Thus, if a molecule bounces elastically against a piston that is moving towards it, it will gain kinetic energy, and it will lose kinetic energy if it bounces off a piston that is moving away from it.



Let us calculate the work done by a mole of an ideal gas in a reversible adiabatic expansion from  $(P_1, V_1)$  to  $(P_2, V_2)$ :

$$W = \int_{V_1}^{V_2} P dV. \quad 8.4.6$$

For a reversible adiabatic expansion,  $PV^\gamma = K$ , and therefore

$$W = K \int_{V_1}^{V_2} V^{-\gamma} dV = \frac{K}{\gamma-1} (V_1^{-(\gamma-1)} - V_2^{-(\gamma-1)}). \quad 8.4.7$$

That is, 
$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{R(T_1 - T_2)}{\gamma - 1}. \quad 8.4.8$$

(Note that  $T_2 < T_1$  in this adiabatic expansion.)

Compare this with equation 8.3.1 for an isothermal expansion.

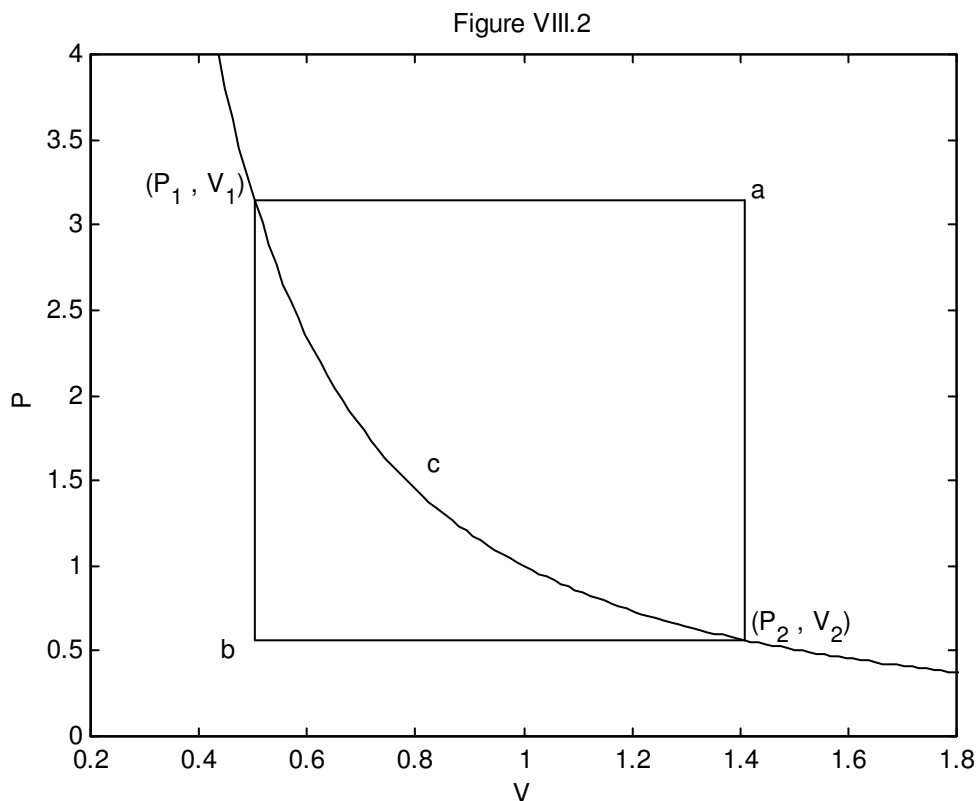
Note also that, since  $R = C_p - C_v$  and  $C_p/C_v = \gamma$ , this can also be written

$$W = C_v(T_1 - T_2). \quad 8.4.9$$

This is also equal to the heat that would be lost if the gas were to cool from  $T_1$  to  $T_2$  at constant volume. Think about this! Is it coincidence, or must it be so?

Here is a useful *exercise*. In figure VIII.2, a gas goes from  $(P_1, V_1)$  to  $(P_2, V_2)$  via three different reversible routes:

- An isobaric expansion followed by an isochoric decrease in pressure;
- An isochoric decrease in pressure followed by an isobaric expansion;
- An adiabatic expansion.





At each stage, calculate the work done **on** or **by** the gas, the heat gained **by** the gas or lost **from** the gas, and the **increase** or **decrease** of the internal energy of the gas. This exercise will illustrate that  $U$  is a function of state, but  $Q$  and  $W$  are not. (I expect the answers to be in algebra; ignore the numbers on the axes – they don't mean anything in particular.)

### 8.5 The Clément-Desormes Experiment

This is a simple, quick and effective experiment often seen in teaching laboratories for measuring  $\gamma$  for air, or, with some extra effort, any other gas.

Sometimes this experiment is referred to as the experiment of Clément and Desormes, and sometimes as the experiment of Clément-Desormes. Apparently Charles-Bernard Desormes was the uncle of Nicolas Clément, and they both worked on the experiment. Nicolas Desormes later legally changed his name to Nicolas Clément-Desormes. Thus you can refer either to the experiment of Clément and Desormes or to the experiment of Clément-Desormes!

A bottle of air starts at  $P_1, T_1$ .  $P_1$  is a little greater than atmospheric pressure  $P_0$ .  $T_1$  is the ambient room temperature. The bottle is provided with some device for measuring pressure (for example, a manometer). We'll see that there is no need to measure temperatures. The stopcock is quickly opened and immediately closed. The pressure at that moment is just atmospheric pressure, which I'll call  $P_0$ , and the temperature is  $T_2$ , which is a little cooler than the original room temperature  $T_1$ . The bottle of gas is now allowed slowly to warm up isochorically to its original temperature  $T_1$ , by which time the new pressure  $P_2$  is greater than atmospheric pressure  $P_0$  but not as large as the original pressure  $P_1$ . You should sketch these two stages on a  $PV$  diagram.

$$\text{For the adiabatic process,} \quad P_1^{-(\gamma-1)} T_1^\gamma = P_0^{-(\gamma-1)} T_2^\gamma. \quad 8.5.1$$

$$\text{For the isochoric process,} \quad P_0 / T_2 = P_2 / T_1. \quad 8.5.2$$

I'll leave you to do the algebra and eliminate  $T_2 / T_1$  from these equations and hence show that

$$\gamma = \frac{\ln(P_1 / P_0)}{\ln(P_1 / P_2)}. \quad 8.5.3$$

In the above analysis, we assumed that the gas was ideal and the expansion was adiabatic and reversible. The gas is nearly ideal if it is a long way above its critical temperature and there are no enormous ranges of  $P$  and  $T$ . The expansion is adiabatic if  $P_2$  is measured immediately after the stopcock is opened and closed, so that there is no time for heat to enter or leave the system. It is reversible only if  $P_1 - P_0 \ll P_0$ .

If you want to do the experiment yourself right now without getting up from your comfortable seat, have a look at <http://www.univ-lemans.fr/enseignements/physique/02/thermo/clement.html>

### 8.6 The Slopes of Isotherms and Adiabats

For an ideal gas in an isothermal process,  $PV = \text{constant}$ .

In a reversible adiabatic process:

$$PV^\gamma = \text{constant}, \quad TV^{\gamma-1} = \text{constant}, \quad P^{1-\gamma}T^\gamma = \text{constant}.$$

From these it is easy to see that the ratios of the adiabatic, isothermal, isobaric and isochoric slopes are as follows:

$$\left(\frac{\partial P}{\partial V}\right)_s = \gamma \left(\frac{\partial P}{\partial V}\right)_T; \quad \left(\frac{\partial V}{\partial T}\right)_s = -\frac{1}{\gamma-1} \left(\frac{\partial V}{\partial T}\right)_P; \quad \left(\frac{\partial P}{\partial T}\right)_s = \frac{\gamma}{\gamma-1} \left(\frac{\partial P}{\partial T}\right)_V.$$

8.6.1a,b,c

For example: - isothermal:  $PV = \text{constant}$ . Take logarithms and differentiate:  $\frac{dP}{P} + \frac{dV}{V} = 0$ . Hence

$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}$ . adiabatic:  $PV^\gamma = \text{constant}$ . Take logarithms and differentiate:  $\frac{dP}{P} + \gamma \frac{dV}{V} = 0$ . Hence

$\left(\frac{\partial P}{\partial V}\right)_s = -\gamma \frac{P}{V}$ . The other two relations can be obtained in a similar manner.

Do these relations hold in general for any equation of state, or are they valid only for an ideal gas? In this section, we shall see that they are valid in general for any equation of state, and are not restricted to the equation of state for an ideal gas.

Let us imagine that the state of the working substance (be it gas, liquid or solid) starts in  $PVT$  space at point A ( $P, V, T_A$ ). We are going to take it to a new point B ( $P + \delta P, V + \delta V, T_B$ ). As I have drawn it in Figure VIII.3,  $\delta P$  is positive,  $\delta V$  is negative, and  $T_B > T_A$ .

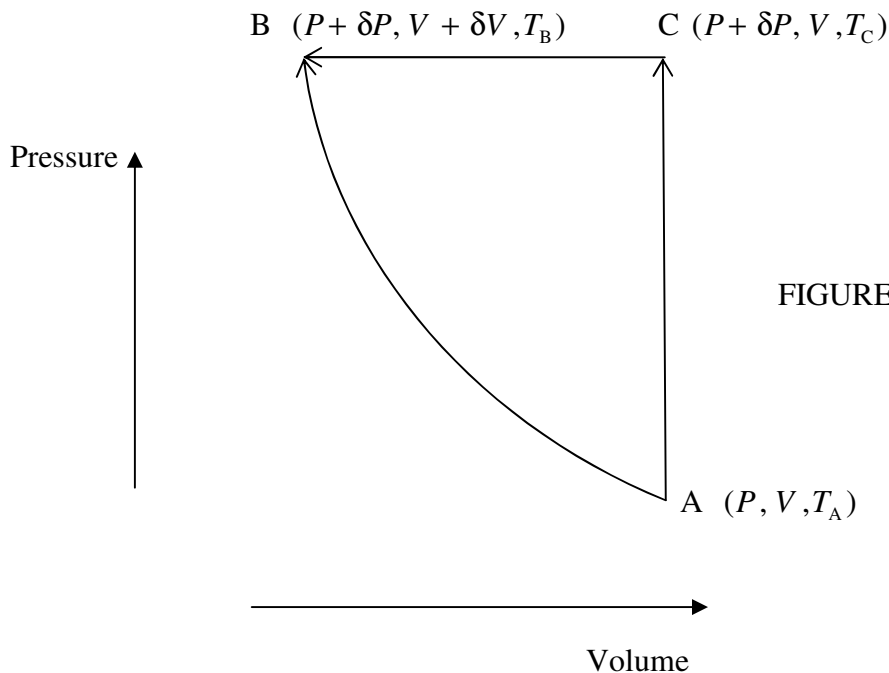


FIGURE VIII.3

We first suppose that we make this move by a *single, adiabatic process*. In that case no heat is added to or lost from the system, and *the increase in the internal energy is  $-P\delta V$* .

Alternatively, B can be reached in two stages:

An isochoric path from A to a new point C ( $P + \delta P$ ,  $V$ ,  $T_C$ ), followed by

An isobaric path from C to B.

As I have drawn it in Figure VIII.3,  $T_C > T_B > T_A$ .

In the *isochoric process*, no work is done by or on the system, and *the increase in the internal energy is equal to the heat added to the system*,  $C_V(T_C - T_A)$ .

In the *isobaric process*, *the increase in the internal energy is equal to the work done on the system*,  $-P\delta V$ , *minus the heat lost from the system*,  $C_P(T_C - T_B)$ ; that is,  $-C_P(T_C - T_B) - P\delta V$ .

Therefore, since the total increase in internal energy is route-independent,

$$-P\delta V = C_V(T_C - T_A) - C_P(T_C - T_B) - P\delta V. \quad 8.6.2$$

Cancel  $P\delta V$  and write  $\gamma$  for  $C_P/C_V$ , so that

$$(T_C - T_A) = \gamma(T_C - T_B). \quad 8.6.3$$

$$\text{But } T_C = T_A + \left(\frac{\partial T}{\partial P}\right)_V \delta P \quad \text{and} \quad T_B = T_C + \left(\frac{\partial T}{\partial V}\right)_P \delta V.$$

[Reminder: Here  $\delta P$  means  $P_C - P_A$  (which, in the way in which I have drawn it in figure VIII.3, is positive) and  $\delta V$  means  $V_B - V_C$  (which, in the way in which I have drawn it in figure VIII.3, is negative).]

$$\text{Therefore} \quad \left(\frac{\partial T}{\partial P}\right)_V \delta P = -\gamma \left(\frac{\partial T}{\partial V}\right)_P \delta V. \quad 8.6.4$$

Divide both sides by  $\delta V$  and go to the infinitesimal limit, recalling that  $\delta P$  and  $\delta V$  are related through an adiabatic path:

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_S = -\gamma \left(\frac{\partial T}{\partial V}\right)_P. \quad 8.6.5$$

$$\text{Therefore} \quad \left(\frac{\partial P}{\partial V}\right)_S = -\gamma \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V. \quad 8.6.6$$

But  $\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T = -1$ , so  $\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T$ .

Therefore 
$$\left(\frac{\partial P}{\partial V}\right)_S = \gamma \left(\frac{\partial P}{\partial V}\right)_T. \quad 8.6.7$$

Thus, as for the ideal gas, the slope of the adiabat is  $\gamma$  times the slope of the isotherm, only this time we have made no assumption about the equation of state.

The other two relations (equations 8.6.1 b,c) can be dealt with as follows.

Equation 8.6.3 can be rearranged to read

$$T_B - T_A = -(\gamma - 1)(T_B - T_C). \quad 8.6.8$$

But  $T_B = T_A + \left(\frac{\partial T}{\partial V}\right)_S \delta V$  and  $T_B = T_C + \left(\frac{\partial T}{\partial V}\right)_P \delta V$ .

Hence 
$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{1}{\gamma - 1} \left(\frac{\partial V}{\partial T}\right)_P, \quad 8.6.9$$

which is the same as equation 8.6.1 b, but without any assumption about the equation of state.

Note also that

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1. \quad 8.6.10$$

Combine this with equations 8.6.7 and 8.6.9 to obtain

$$\frac{1}{\gamma} \left(\frac{\partial P}{\partial V}\right)_S \cdot (\gamma - 1) \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial P}\right)_V = 1. \quad 8.6.11$$

Therefore 
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\gamma - 1}{\gamma} \left(\frac{\partial P}{\partial V}\right)_S \left(\frac{\partial V}{\partial T}\right)_S = \frac{\gamma - 1}{\gamma} \left(\frac{\partial P}{\partial T}\right)_S. \quad 8.6.12$$

Therefore 
$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{\gamma}{\gamma - 1} \left(\frac{\partial P}{\partial T}\right)_V, \quad 8.6.13$$

which is the same as equation 8.6.1 c, but without any assumption about the equation of state.

### 8.7 Scale Height in an Isothermal Atmosphere

The material in this chapter doubtless has countless applications, most of which I am unaware of, in meteorology. Two simple topics are easy to mention, namely the *scale height in an isothermal atmosphere*, dealt with in this section, and the adiabatic lapse rate dealt with in the next section.

Let us imagine a column of air of cross-sectional area  $A$  in an isothermal atmosphere – that is to say the temperature  $T$  is uniform throughout. Consider the equilibrium of the portion of the air between heights  $z$  and  $z + dz$ . The weight of this portion is  $\rho g A dz$ . Let  $P$  be the pressure at height  $z$  and  $P + dP$  be the pressure at height  $z + dz$ . (Note that  $dP$  is negative.) The net upward force on the portion  $dz$  of the air is  $-AdP$ . Therefore  $dP = -\rho g dz$ .

But if we regard air as an ideal gas, it obeys the equation of state for an ideal gas, equation 6.1.7:  $P = \rho RT / \mu$ , where  $\rho$  and  $\mu$  are respectively the density and the “molecular weight” (molar mass)

of the gas. Therefore  $\frac{RT}{\mu} d\rho = -\rho g dz$ , or  $\frac{d\rho}{\rho} = -\frac{\mu g}{RT} dz$ .

Integrate to obtain  $\rho = \rho e^{-z/H}$ , 8.7.1

where  $H = \frac{RT}{\mu g}$  is the *scale height*. It is large if the

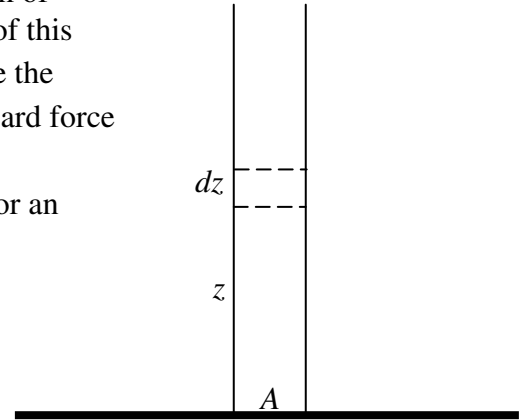


FIGURE VIII.4

temperature is high, the gas light and the planet’s gravity feeble. It is the height at which the density is reduced to a fraction  $1/e$ , or 36.8% of its ground value. What would it be, in kilometres, for an atmosphere consisting of 80%  $N_2$  and 20%  $O_2$ , at a temperature of 20 °C, where the gravitational acceleration is  $9.8 \text{ m s}^{-2}$ ? What fraction is this of the radius of Earth? If you made a model of Earth one metre in diameter (radius = 50 cm), how thick would be the atmosphere? You’d better look after it - our atmosphere is a very thin skin clinging to the surface!

### 8.8 Adiabatic Lapse Rate

Earth’s atmosphere is not, of course, isothermal. The temperature decreases with height. The temperature *lapse rate* in an atmosphere is the rate of decrease of temperature with height; that is to say, it is  $-dT/dz$ .

An *adiabatic* atmosphere is one in which  $P/\rho^\gamma$  does not vary with height. In such an atmosphere, if a lump of air is moved adiabatically to a higher level, its pressure and density will change so that  $P/\rho^\gamma$  is constant – and will be equal to the ambient pressure and density at the new height. For such an atmosphere, it is possible to calculate the rate at which temperature decreases with height – the *adiabatic lapse rate*. We shall do this calculation, and see how it compares with actual lapse rates.

As in Section 8.7, the condition for hydrostatic equilibrium is

$$dP = -\rho g dz. \quad 8.8.1$$

Since we are trying to find a relation between  $T$  and  $z$  for an adiabatic atmosphere (i.e. one in which  $P/\rho^\gamma$  doesn't vary with height), we need to find the adiabatic relations between  $P$  and  $T$  and between  $\rho$  and  $T$ .

These are easily found from the adiabatic relation between  $P$  and  $\rho$ :

$$P = c\rho^\gamma \quad 8.8.2$$

and the ideal gas equation of state:

$$P = \frac{\rho RT}{\mu}. \quad 8.8.3$$

Eliminate  $P$ :

$$\rho = \left( \frac{RT}{c\mu} \right)^{1/(\gamma-1)}. \quad 8.8.4$$

Eliminate  $\rho$ :

$$P = \frac{R^{\gamma/(\gamma-1)}}{\mu^{\gamma/(\gamma-1)} c^{1/(\gamma-1)}} T^{\gamma/(\gamma-1)}, \quad 8.8.5$$

from which

$$dP = \frac{\gamma}{\gamma-1} \frac{R^{\gamma/(\gamma-1)}}{\mu^{\gamma/(\gamma-1)} c^{1/(\gamma-1)}} T^{1/(\gamma-1)} dT. \quad 8.8.6$$

Substitute equations (8.8.4) and (8.8.6) into equation (8.8.1), to obtain, after a little algebra, the following equation for the adiabatic lapse rate:

$$-\frac{dT}{dz} = \left( 1 - \frac{1}{\gamma} \right) \frac{g\mu}{R}. \quad 8.8.7$$

This is independent of temperature.

If you take the mean molar mass for air to be  $28.8 \text{ kg kmole}^{-1}$ , and  $g$  to be  $9.8 \text{ m s}^{-2}$  for temperate latitudes, you get for the adiabatic lapse rate for dry air  $-9.7 \text{ K km}^{-1}$ . The presence of water vapour in humid air reduces the mean value of  $\mu$  (and hence the adiabatic lapse rate), and actual lapse rates are usually rather less than the calculated adiabatic lapse rates even for humid air. (The presence of

water vapour also increases slightly the value of  $\gamma$ . This would result in a slightly larger lapse rate, but the effect is not as great as the reduction in lapse rate caused by the larger value of  $\mu$ . Try some numbers to convince yourself of this.) The International Civil Aviation Organization Standard Atmosphere takes the lapse rate in the troposphere (first 11 km) to be  $-6.3 \text{ K km}^{-1}$ . What happens if the actual lapse rate is faster than the adiabatic lapse rate? If you imagine a lump of air to be moved adiabatically to a higher level, its pressure and density will change so that  $P/\rho^\gamma$  is constant, and it will then find itself in a region where its new density is less than the new ambient density. Consequently, it will continue to rise, and the atmosphere will be convectively unstable, and a storm will ensue. The atmosphere is stable as long as the actual lapse rate is less than the adiabatic lapse rate (which is reduced in humid air) is unstable if the actual lapse rate is greater than the adiabatic lapse rate.

### 8.9 Numerical Values of Specific and Molar Heat Capacities

The following table is not intended as a definitive, authoritative table of precise heat capacities. It is intended just to give a rough idea of the orders of magnitude and the relative magnitudes for a few substances.

For gases, the heat capacities tabulated are at *constant pressure*. For solids and liquids the difference between  $C_p$  and  $C_v$  is much smaller than for gases, because of the much smaller coefficient of expansion. Notice that the molar heat capacities for gases, when expressed in terms of  $R$ , are about what are expected from the theoretical considerations in this chapter. Notice the relatively large molar heat capacities of organic liquids (the molecules can rotate and can vibrate in many modes), and that, the more complex the molecule, the larger its molar heat capacity. Notice, however, that, because water has a low molecular weight (molar mass), water has the largest *specific* heat capacity of any common liquid or solid. (The specific heat capacities of gaseous  $\text{H}_2$  and He are, unsurprisingly, larger still. A kilogram of hydrogen is an enormous number of molecules, so it takes a lot of heat to warm them all up.) We have not studied the theory of the heat capacities of solids in this chapter, but, when you do so in a course on solid state physics or on statistical mechanics, you will understand that the expected molar heat capacity of metals would be about  $3R$ , which is approximately what is shown for the three metals in this table.

		Specific Heat Capacity at Constant Pressure		Molar Heat Capacity at Constant Pressure	
		cal g <sup>-1</sup> C° <sup>-1</sup>	J kg <sup>-1</sup> K <sup>-1</sup>	J kmole <sup>-1</sup> K <sup>-1</sup>	In units of <i>R</i>
Helium	(g)	1.25	5250	21000	2.53 <i>R</i>
Argon	(g)	0.13	526	21000	2.53 <i>R</i>
H <sub>2</sub>	(g)	3.44	14400	28800	3.46 <i>R</i>
O <sub>2</sub>	(g)	0.22	919	29400	3.54 <i>R</i>
N <sub>2</sub>	(g)	0.25	1040	29100	3.50 <i>R</i>
CO <sub>2</sub>	(g)	0.20	843	37100	4.46 <i>R</i>
H <sub>2</sub> O	(l)	1	4184	75300	9.1 <i>R</i>
C <sub>2</sub> H <sub>5</sub> OH	(l)	0.58	2430	112000	13.5 <i>R</i>
CCl <sub>4</sub>	(l)	0.20	852	131000	15.8 <i>R</i>
C <sub>6</sub> H <sub>6</sub>	(l)	0.42	1740	136000	16.4 <i>R</i>
Al	(s)	0.22	941	25400	3.1 <i>R</i>
Cu	(s)	0.092	384	24400	2.9 <i>R</i>
Fe	(s)	0.11	450	25100	3.0 <i>R</i>

### 8.10 Heat Capacities of Solids

I do not deal a great deal with solid state physics in these notes, particularly in this chapter, which has been concerned mostly with gases. But the inclusion of the heat capacities of three metals in the above table provides an opportunity for a brief mention of the heat capacities of metals and of other crystalline solids. In a simple model of a crystalline solid, the solid can be thought of as a regular lattice of atoms held in position near their neighbours by springs, and the atoms have three degrees of vibrational freedom – in the *x*, *y* and *z* directions. For each of these vibrational modes there are two squared terms (of the form  $\frac{1}{2}mv^2$  and  $\frac{1}{2}I\omega^2$ ) that contribute to the internal energy. The internal energy associated with each of these six terms is  $\frac{1}{2}RT$  per mole, which comes to  $3RT$  per mole, and thus you would expect the molar heat capacity to be about  $3R$  – and you can see from the above table that this is indeed the case. Indeed at room temperature, most metals and simple crystalline solids have a molar heat capacity of about  $3R$ . (This is sometimes referred to as



“Dulong and Petit’s Rule”.) At low temperatures, however, the molar heat falls below this value, and eventually approaches zero at 0 K. At very low temperatures, the molar heat capacity varies roughly as the cube of the temperature. As room temperatures are reached, the molar heat capacity asymptotically approaches the “classical” value of  $3R$ .

The run of molar heat capacity with temperature at low temperatures looks a little like figure VIII.5 for magnesium and figure VIII.6 for silver bromide. It will be seen that these two curves are the same shape except for a different scale along the temperature axis – and the same is true for most metals and simple crystalline solids. Indeed we can assign to each solid a characteristic temperature, known as the *Debye temperature*,  $\theta_D$ , and then, if we express temperature not in kelvin but in units of the Debye temperature for the particular solid, then the curves are indeed the same shape. In other words, the molar heat capacity of all solids (or at least all solids that behave like this!) is the same function of  $T/\theta_D$ . I show this function as figure VIII.7.

The theory of the heat capacities of solids was investigated by Einstein and by Debye. (Peter Debye – Dutch-American physicist/chemist. Nobel Chemistry prize 1936.) The Debye temperature is related to the vibrational frequency of the atoms in their crystalline lattice. Diamond is a very hard substance, with very strong interatomic bonds. Consequently the vibrational frequencies are very high, and the Debye temperature for diamond is correspondingly high:  $\theta_D = 1860$  K. As a result of this the heat capacity rises very slowly with increasing temperature, and at room temperature is well below the “classical” value of  $3R$ . Most other solids have weaker bonds and far lower Debye temperatures, and consequently their molar heat capacities have almost reached the classical Dulong-Petit value of  $3R$  at room temperature. Here are a few Debye temperatures:

Potassium:	100 K
Silver bromide	145
Silver	215
Magnesium	290
Copper	315
Iron	420

If it seems that the harder the solid the higher the Debye temperature and the slower the solid is to reach its classical  $C_V$  of  $3R$ , this is not coincidence.

I do not derive Debye’s theoretical formula here – it is something to look forward to in courses on solid state physics or statistical mechanics, but, for interest, the formula (which I used for calculating figures VIII.5-7) is

$$C_V = 9T^3 \int_0^{1/T} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad 8.9.1$$

In this equation  $C_V$  is in units of  $R$ , and  $T$  is in units of the Debye temperature.

FIGURE VIII.5

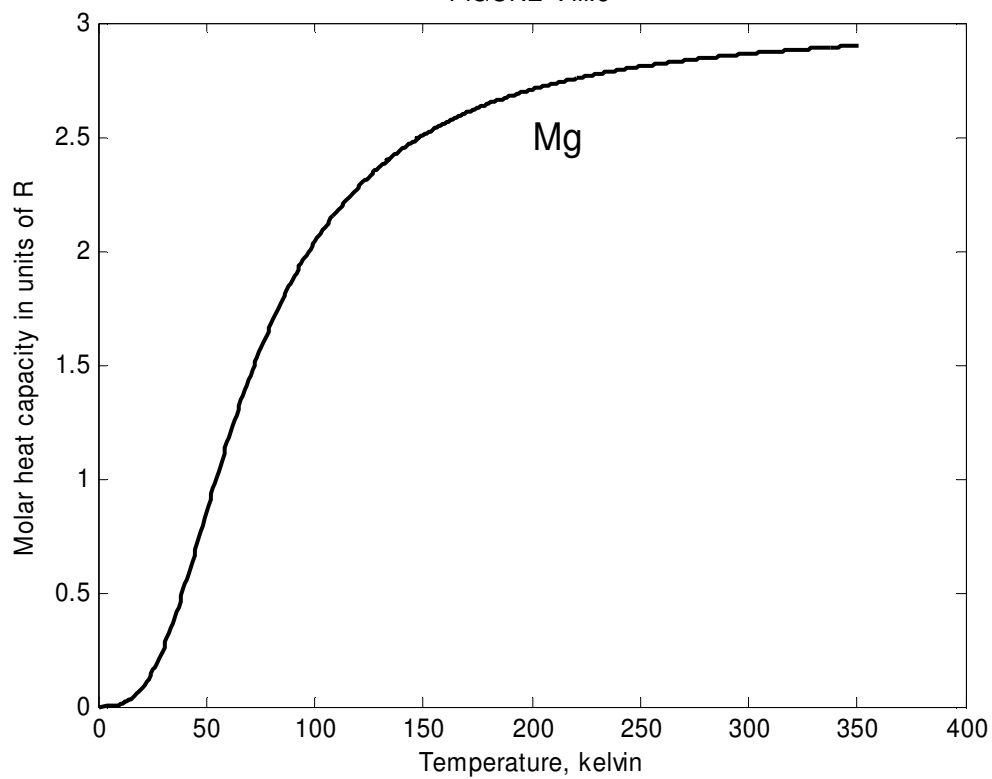
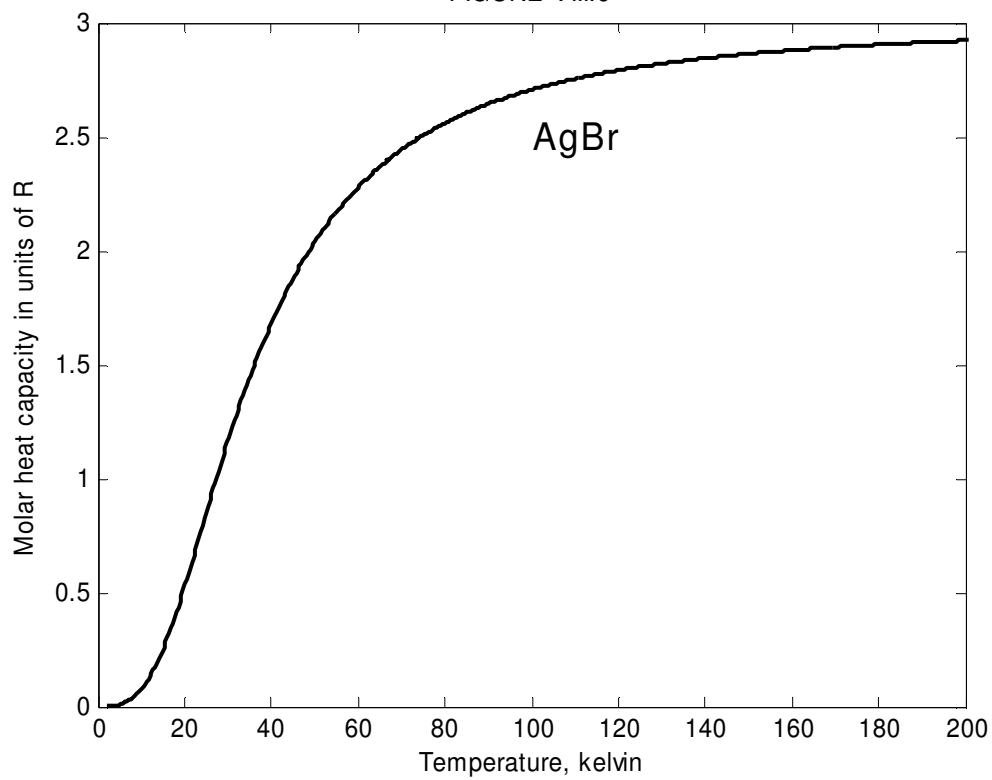
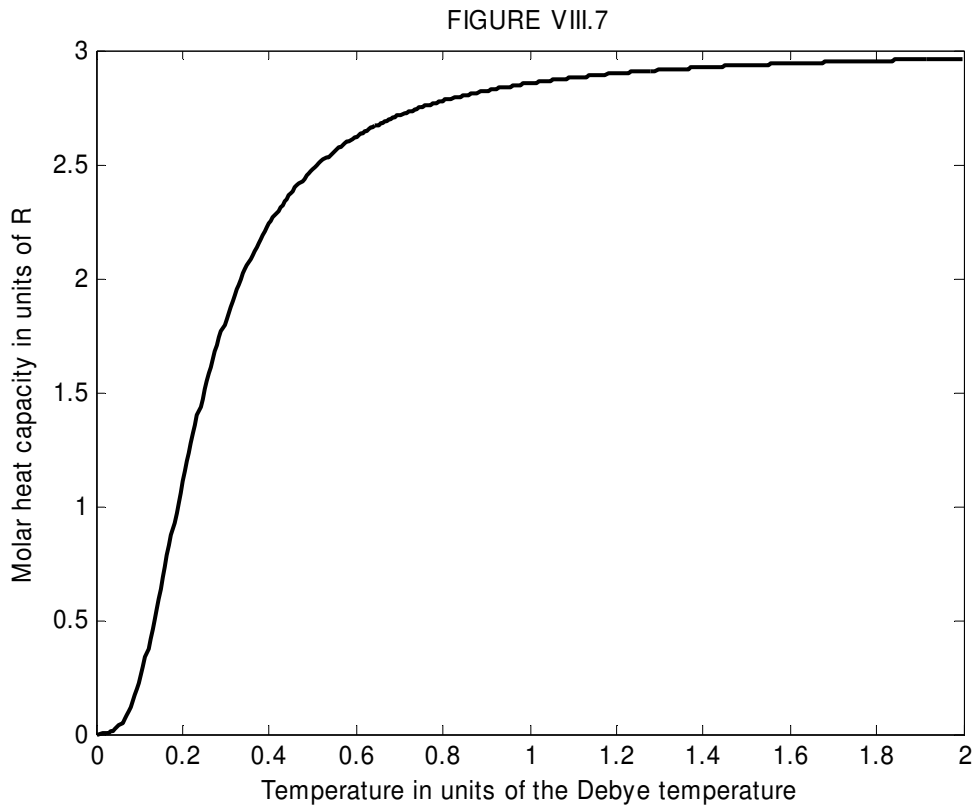


FIGURE VIII.6





In case you are wondering what the symbol “ $x$ ” stands for in equation 8.9.1, it is merely a dummy variable, for the integral in that expression is a function not of  $x$  but of  $T$ , the upper limit of the integral.

If you try to reproduce figure VIII.7 yourself by evaluating equation 8.9.1 for a number of different temperatures, you will soon find that it is a good deal more laborious than may at first be evident.

In my first attempt at doing it, for each of the 400 values of  $T$  that I used for plotting Figure VIII.7, I used a 1000 point Simpson’s Rule integration. Thus I evaluated the integrand 400,000 times, and it took the computer almost half a second. Later, I found that Gaussian quadrature was much, much more efficient, requiring the calculation of the integrand at only a very few points.

However, J. Viswanathan of Chennai, India, has since shown me an even better method than the Gaussian quadrature.

He uses the theorem  $\frac{d}{dx} \int_0^{g(x)} f(y) dy = f(g(x))g'(x)$ . This was a new one on me, but it is very easy to derive and looks almost obvious in hindsight. Applied to our problem, that is, applied to our equation

$$C_V = 9T^3 \int_0^{1/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad 8.9.1$$

it becomes, after a modest amount of work:

$$\frac{dC_V}{dT} = \frac{3C_V}{T} - 9Tf(1/T), \quad 8.9.2$$

where

$$f(x) = \frac{x^4 e^x}{(e^x - 1)^2}. \quad 8.9.3$$

He evaluates  $C_V$  at  $T = 2$ , using a direct numerical integration of equation 8.9.1 - but this is the *only* time that he does this! The answer is 2.9628. Then he moves down by  $dT$  at each step and calculates the corresponding  $dC_V$  by using a fourth order Runge-Kutta integration on the differential equation 8.9.3. The three methods agree very well, but the Simpson's Rule method was by far the most laborious.

Debye's theory was published in 1912, and they certainly didn't have electronic computers, or even electronic hand calculators, in those days. In the 1950s most scientists were using hand-operated mechanical calculators, with electrically-driven mechanical calculators beginning to come into use towards the end of that decade. I suspect that in 1912 not even hand-operated mechanical calculators were available, and calculations would have been done using pencil and paper and logarithm and other tables. One must think of the physical insight and mathematical competence needed to develop the theory of the heat capacity in the first place, and then the enormous effort needed to calculate the resulting equations.