

## CHAPTER 13

### EXPANSION, COMPRESSION AND THE $TdS$ EQUATIONS

#### 13.1 *Coefficient of Expansion*

Notation: In an ideal world, I'd use  $\alpha$ ,  $\beta$ ,  $\gamma$  respectively for the coefficients of linear, area and volume expansion. Unfortunately we need  $\gamma$  for the ratio of heat capacities. Many people use  $\beta$  for volume expansion, so I'll follow that. What, then, to use for area expansion? I'll use  $b$ , so we now have  $\alpha$ ,  $b$ ,  $\beta$ , which is very clumsy. However, we shall rarely need  $b$ , so maybe we can survive.

Coefficient of linear expansion:  $\alpha$   
 Coefficient of area expansion:  $b$   
 Coefficient of volume expansion:  $\beta$

For small ranges of temperature, the increases in length, area and volume with temperature can be represented by

$$l_2 = l_1[1 + \hat{\alpha}(T_2 - T_1)], \quad 13.1.1$$

$$A_2 = A_1[1 + \hat{b}(T_2 - T_1)] \quad 13.1.2$$

and 
$$V_2 = V_1[1 + \hat{\beta}(T_2 - T_1)]. \quad 13.1.3$$

Here  $\hat{\alpha}$ ,  $\hat{b}$  and  $\hat{\beta}$  are the approximate *coefficients of linear, area and volume expansion* respectively over the temperature range  $T_1$  to  $T_2$ . For all three, the units are degree<sup>-1</sup> – that is C°<sup>-1</sup> or K<sup>-1</sup>.

For anisotropic crystals, the coefficient may be different in different directions, but for isotropic materials we can write

$$A_2 = l_2^2 = l_1^2[1 + \hat{\alpha}(T_2 - T_1)]^2 = A_1[1 + 2\hat{\alpha}(T_2 - T_1) + \dots] \quad 13.1.4$$

$$V_2 = l_2^3 = l_1^3[1 + \hat{\alpha}(T_2 - T_1)]^3 = V_1[1 + 3\hat{\alpha}(T_2 - T_1) + \dots]. \quad 13.1.5$$

Thus for small expansions,  $\hat{b} \approx 2\hat{\alpha}$  and  $\hat{\beta} \approx 3\hat{\alpha}$ .

Equations 13.1.1, 2 and 3 define the approximate coefficients over a finite temperature range. *The coefficients at a particular temperature* are defined in terms of the derivatives, i.e.

$$\alpha = \frac{1}{l} \left( \frac{\partial l}{\partial T} \right)_p, \quad 13.1.6$$

$$b = \frac{1}{A} \left( \frac{\partial A}{\partial T} \right)_p \quad 13.1.7$$

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p. \quad 13.1.8$$

The relations  $b = 2\alpha$  and  $\beta = 3\alpha$  are exact.

We specify “at constant pressure” because obviously we don’t want, in our definition, to prevent the material from expanding by increasing the pressure on it when we heat it.

For solids, the coefficient of linear expansion is usually the appropriate parameter; for liquids and gases the volume coefficient is usually appropriate. For most familiar common metals the coefficient of linear expansion is of order  $10^{-5} \text{ K}^{-1}$ . Alloys such as the nickel-steel alloy, “invar”, used in clock construction, may have much smaller coefficients. Ordinary glass has a coefficient only a little less than that of metals; pyrex and fused quartz have a much smaller expansion – hence their use in telescope mirrors. For liquids and gases it is usually the volume coefficient that is quoted. The volume coefficient of mercury is about  $0.00018 \text{ K}^{-1}$ . Water actually contracts between 0 and 4 °C, and expands above that temperature. The volume coefficient of air at 0 °C is  $0.0037 \text{ K}^{-1}$ .

At room temperatures and above, the coefficient of linear expansion of metals doesn’t vary a huge amount with temperature, but at low temperatures the coefficient of expansion varies much more rapidly with temperature – and so does the specific heat capacity (see Section 8.10). Indeed, for a given metal, the variation of expansion coefficient and the specific heat capacity vary with temperature in a rather similar manner, so that, for a given metal, the ratio  $\alpha/C_p$  is constant over a large temperature range.

*Exercise:* A square metal plate has a circular hole of area  $300 \text{ cm}^2$  in the middle of it. If the coefficient of linear expansion is  $2 \times 10^{-5} \text{ C}^{-1}$ , calculate the area of the hole when the temperature of the plate is raised through 100 degrees.

*Exercise:* Show that the coefficient of volume expansion of an ideal gas is  $1/T$ . Compare this with the numerical value for air given above.

Although classical thermodynamics does not deal with detailed microscopic processes, it is of interest to ask *why* a solid material expands upon heating. Let us imagine a crystalline solid to be made up of atoms connected to each other by little springs, and each spring is governed by Hooke’s Law, and consequently each atom is vibrating in a parabolic potential well and is moving in simple harmonic motion. If we increase the temperature, we increase the *amplitude* of the vibrations, but we *do not change the mean*

*positions of the atoms.* Consequently, in such a model, we would not expect any expansion upon heating. However, the real potential is not parabolic, but is shaped, at least qualitatively, something like the Lennard-Jones or Morse potentials mentioned in Chapter 6, Section 6.8. If the material is heated, the amplitude of the vibrations increases, and, because of the higher-order terms in the potential, which give the potential its asymmetric anharmonic shape, the mean separation of the atoms does indeed increase, and so we have expansion. Thus the expansion upon heating of a solid material is a consequence of the anharmonicity of the atomic vibrations and the asymmetry of the potential in which they are moving.

In the next two exercises, I shall be thinking of the expansion of a metal rod as the temperature is increased, and the pressure will be assumed to be constant at all times. Thus I am going to assume that pressure is not a variable in the discussion, and I shall define the coefficient of linear expansion as  $\alpha = \frac{1}{l} \frac{dl}{dT}$  rather than the more general  $\frac{1}{l} \left( \frac{\partial l}{\partial T} \right)_P$ . A small point that I make at this stage is this: Suppose that the length of a

metal rod increases linearly with temperature, so that  $\frac{dl}{dT}$  is independent of temperature.

It will occur to the reader, on looking at the definition  $\alpha = \frac{1}{l} \frac{dl}{dT}$  that this does *not* mean that the coefficient of expansion is independent of temperature. And if  $\alpha$  is independent of temperature,  $l$  does *not* increase linearly with temperature. The next two exercises will illustrate that, and will also illustrate how the exact coefficient  $\alpha = \frac{1}{l} \frac{dl}{dT}$  is related to what I have called (for want of a better term) the “approximate” coefficient  $\bar{\alpha} = \frac{1}{l_1} \frac{l_2 - l_1}{T_2 - T_1}$ .

*Exercise.* Suppose that the length of a metal rod increases with temperature according to  $l = l_0(1 + \alpha_0 T)$ , where  $l_0$  is the length at 0 K, and  $\alpha_0$  is the coefficient at 0 K. This means that  $\frac{dl}{dT}$  and  $l\alpha$  are independent of temperature, and each is equal to  $l_0\alpha_0$ . Show that the coefficient at temperature  $T$  is given by

$$\alpha = \frac{\alpha_0}{1 + \alpha_0 T}.$$

Show also that  $\bar{\alpha}$ , the approximate coefficient over the temperature range  $T_1$  to  $T_2$ , is equal to the exact coefficient  $\alpha$  evaluated at  $T = T_1$ .

*Exercise.* Suppose that the coefficient  $\alpha$  is independent of temperature. Show that the length of the rod increases with temperature according to

$$l = l_0 e^{\alpha T},$$

where  $l_0$  is the length at 0 K. Show also that

$$\hat{\alpha} = \frac{e^{\alpha(T_2 - T_1)} - 1}{T_2 - T_1}.$$

By this time, it may have occurred to the reader that what we have called  $\hat{\alpha}$ , for all its usefulness in the equation  $l_2 = l_1[1 + \hat{\alpha}(T_2 - T_1)]$ , is not “the” coefficient of expansion at temperature  $T_1$ , nor is it the *mean* coefficient in the temperature range  $T_1$  to  $T_2$ . The *mean* coefficient in this range must be defined by  $\bar{\alpha}(T_2 - T_1) = \int_{T_1}^{T_2} \alpha dT$ . So now, one more exercise:

*Exercise.* Suppose that the length of a metal rod increases with temperature according to

$l = l_0(1 + \alpha_0 T)$ , where  $l_0$  is the length at 0 K, and  $\alpha_0$  is the coefficient at 0 K. Show that

$$\bar{\alpha} = \frac{1}{(T_2 - T_1)} \ln\left(\frac{1 + \alpha_0 T_2}{1 + \alpha_0 T_1}\right).$$

*Summary*

If $\frac{dl}{dT}$ is constant	If $\alpha$ is constant
$l = l_0(1 + \alpha_0 T)$ $\alpha = \frac{\alpha_0}{1 + \alpha_0 T}.$ $\hat{\alpha} = \alpha_1$ $\bar{\alpha} = \frac{1}{(T_2 - T_1)} \ln\left(\frac{1 + \alpha_0 T_2}{1 + \alpha_0 T_1}\right)$	$l = l_0 e^{\alpha T}$ $\alpha = \alpha_0$ $\hat{\alpha} = \frac{e^{\alpha(T_2 - T_1)} - 1}{T_2 - T_1}.$ $\bar{\alpha} = \alpha$

Of course, you may feel that this distinction between  $\alpha$ ,  $\alpha_0$ ,  $\hat{\alpha}$  and  $\bar{\alpha}$  is splitting hairs. Let us discover for ourselves how much they differ, by putting in some numbers. Let us

suppose that  $\alpha_0 = 1.7 \times 10^{-5} \text{ K}^{-1}$  and that  $l_0 = 1 \text{ m}$ . Then, assuming that  $T_1 = 280 \text{ K}$  ( $6.85 \text{ }^\circ\text{C}$ ) and  $T_2 = 380 \text{ K}$  ( $106.85 \text{ }^\circ\text{C}$ ), we obtain

If  $\frac{dl}{dt}$  is constant

$$l_1 = 1.004760 \text{ m}$$

If  $\alpha$  is constant

$$1.004771 \text{ m}$$

$$\alpha (280 \text{ K}) = 1.691946 \times 10^{-5} \text{ K}^{-1}$$

$$\alpha (280 \text{ K}) = 1.700000 \times 10^{-5} \text{ K}^{-1}$$

$$\bar{\alpha} = 1.691946 \times 10^{-5} \text{ K}^{-1}$$

$$\bar{\alpha} = 1.701446 \times 10^{-5} \text{ K}^{-1}$$

$$\bar{\bar{\alpha}} = 1.690516 \times 10^{-5} \text{ K}^{-1}$$

$$\bar{\bar{\alpha}} = 1.700000 \times 10^{-5} \text{ K}^{-1}$$

In general, if the length at  $T_1$  is  $l_1$ , the length  $l_2$  at  $T_2$  will be given by

$$l_2 = l_1 \exp\left(\int_{T_1}^{T_2} \alpha dT\right). \quad 13.1.9$$

In the case where  $dl/dT$  is constant, so that  $\alpha = \frac{\alpha_0}{1 + \alpha_0 T}$ , this becomes

$$l_2 = l_1 \left( \frac{1 + \alpha_0 T_2}{1 + \alpha_0 T_1} \right) = l_1 \left( 1 + \alpha_0 (T_2 - T_1) - \alpha_0^2 T_1 (T_2 - T_1) + \dots \right) \quad 13.1.10$$

In the case where  $\alpha$  is constant, so it becomes

$$l_2 = l_1 \exp(\alpha(T_2 - T_1)) = l_1 \left( 1 + \alpha(T_2 - T_1) + \frac{1}{2} \alpha^2 (T_2 - T_1)^2 + \dots \right) \quad 13.1.11$$

Thus to the first order of small quantities, all varieties of  $\alpha$  are equal.

*Coefficient of Expansion as a Tensor Quantity.* In Chapter 4, I briefly mentioned that, in the case of an anisotropic crystal, the coefficient of thermal conduction is a tensor quantity. The same is true, for an anisotropic crystal, of the coefficient of expansion. Thus, if, during an physics examination, you were asked to give examples of tensor quantities, you could give these as examples – though a small risk might be involved if your teacher had not thought of these as tensors! The coefficient of expansion of an anisotropic crystal may vary in different directions. (In Iceland Spar – calcium carbonate – in one direction the coefficient is actually negative.) If you cut an anisotropic crystal in the form of a cube, whose edges are not parallel to the crystallographic axis, the sample, upon heating, will not only expand in volume, but it will change in shape to become a non-rectangular parallelepiped. However, it is possible to cut the crystal in the form of a cube such that, upon heating, the sample expands to a rectangular parallelepiped. The edges of the cube (and the resulting parallelepiped) are then parallel to the *principal axes of expansion*, and the coefficients in these directions are the *principal coefficients of expansion*. These directions will be parallel to the crystallographic axes if the crystal has one of more axes of symmetry (but obviously not otherwise).

### 13.2 Compression

The way in which the volume of a material decreases with pressure at constant temperature is described by the *isothermal compressibility*,  $\kappa$ :

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T. \quad 13.2.1$$

Note the necessary minus sign.

Later, we shall need to distinguish between “isothermal compressibility” and “adiabatic compressibility”, and we shall need a subscript to the symbol  $\kappa$  in order to distinguish between the two. For the time being, however,  $\kappa$  with no subscript will be taken to mean the isothermal compressibility.

The reciprocal of  $\kappa$  is called the isothermal *bulk modulus*, sometimes (understandably) called the isothermal *incompressibility*.

*Question:* What are the SI units for compressibility and bulk modulus?

*Exercise:* Show that the isothermal compressibility of an ideal gas is  $1/P$ .

*Exercise:* What is the bulk modulus of air at atmospheric pressure?

### 13.3 Pressure, Temperature and the Difference in Heat Capacities

The way in which the pressure of a material increases with temperature at constant volume is described by  $\left( \frac{\partial P}{\partial T} \right)_V$ .

*Exercise:* By making use of equation 2.4.11, show that

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}. \quad 13.3.1$$

*Exercise:* By making use of equation 10.4.8, show that

$$C_P - C_V = \frac{TV\beta^2}{\kappa} = \frac{9TV\alpha^2}{\kappa}. \quad 13.3.2$$

Thus we can determine  $C_P - C_V$  from measurements of the expansion coefficient and the isothermal compressibility without knowing the equation of state. We have already shown that the expansion coefficient of an ideal gas is  $1/T$ , and the isothermal

compressibility of an ideal gas is  $1/P$ . Note that, for an ideal gas,  $\beta = 1/T$  and  $\kappa = 1/P$ , so that equation 13.3.2 reduces to  $R$ .

Note that, in equation 13.3.2,  $\kappa$  is the isothermal compressibility.  $C_P$  and  $C_V$  may denote the molar heat capacities (in which case  $V$  is the molar volume); or they may denote the specific heat capacities (in which case  $V$  is the specific volume or reciprocal of density); or they may denote the total heat capacities (in which case  $V$  is the total volume).

Recall that the physical reason that  $C_P$  is greater than  $C_V$  is that when a substance is heated and expands at constant pressure, it does work, whereas if held at constant volume it does no work. In the case of an ideal gas expanding reversibly, the work done is all external work. A real gas, or a van der Waals gas, on expanding also does *internal* work against the intermolecular forces. Therefore  $C_P$  is greater than  $C_V$  by more than  $R$  – but only a little more, because the intermolecular (van der Waals) forces are not very large. In Chapter 10 we developed an explicit expression for  $C_P - C_V$  for a van der Waals gas (equation 10.4.10). When a solid is heated, it expands very little compared with a gas, and hence does very little external work. The intermolecular forces, however, are quite large, and hence an expanding solid does quite a lot of internal work. Thus for a gas, most of the work of expansion is external; for a solid, most of the work of expansion is internal.

Here are order-of-magnitude figures for copper at room temperature (for exact figures, we would have to specify the exact temperature).

Specific heat capacity at constant pressure	$= 384 \text{ J K}^{-1} \text{ kg}^{-1}$
Molar mass (“atomic weight”)	$= 63.5 \text{ kg kmole}^{-1}$
Molar heat capacity at constant pressure	$= 24400 \text{ J K}^{-1} \text{ kmole}^{-1} = 2.93 R$ .
Density	$= 8960 \text{ kg m}^{-3}$
Molar volume	$= 7.09 \times 10^{-3} \text{ m}^3 \text{ kmole}^{-1}$
Coefficient of linear expansion	$= 1.67 \times 10^{-5} \text{ K}^{-1}$
Coefficient of volume expansion	$= 5.00 \times 10^{-5} \text{ K}^{-1}$
Isothermal bulk modulus	$= 1.40 \times 10^{11} \text{ Pa}$
Isothermal compressibility	$= 7.14 \times 10^{-12} \text{ Pa}^{-1}$

Equation 13.3.2 will give us, at a temperature of  $20^\circ\text{C} = 293.15 \text{ K}$ ,

$$C_P - C_V \text{ (molar)} = 728 \text{ J K}^{-1} \text{ kmole}^{-1} = 0.09R.$$

$$C_P - C_V \text{ (specific)} = 11 \text{ J K}^{-1} \text{ kg}^{-1}$$

This is only about 3 percent of  $C_P$ .

Equation 13.3.2 raises an interesting problem concerning water. It will be understood that the reason why  $C_P$  for an ideal gas is greater than  $C_V$  is as follows. When heat is added to an ideal gas at constant volume, all of the heat goes into raising the temperature. When heat is added at constant pressure, however, some of the heat goes into doing external work. Hence  $C_P > C_V$ . That argument is correct. However...

Water at 2 °C (or indeed at any temperature in the range between 0 °C and 4 °C) contracts upon heating (i.e.  $\beta$  is negative), so that, if we add heat at constant pressure, work is done on the water by its surroundings, and hence (we might argue, though erroneously), for water at 2 °C,  $C_p < C_v$ . Equation 13.3.2, however, shows that  $C_p \geq C_v$  regardless of the sign of  $\beta$ . (The equality applies where  $\beta = 0$ , which occurs at 4 °C.) Thus we have a paradox.

In fact, equation 13.3.2 is correct, and, at 2 °C,  $C_p > C_v$ . The explanation is as follows. It is true that, when heat is added to an ideal gas at constant volume, all of the heat goes into raising the temperature – but this is true only for an ideal gas in which the internal energy is all kinetic. But for real substances, including water, the correct statement (which is really just the first law of thermodynamics) is that when heat is added to a substance at constant volume, all of the heat goes into raising the *internal energy*, and, for a nonideal substance the internal energy is partly kinetic and partly potential. When we add heat isobarically to water at 2 °C, more of this heat goes into increasing the potential energy than if we add heat isochorically, and hence  $C_p$  is still greater than  $C_v$ . A very clear account of this problem, from both the thermodynamical and statistical mechanical points of view, is to be found in a paper by McDougall and Feistel, *Deep-Sea Research I* **50**, 1523 (2003).

(You may remember a similar apparent paradox in connection with surface tension of a liquid. When we do work adiabatically and reversibly to create new surface, the temperature *drops*. So doing work on a system or adding heat to it doesn't necessarily result in a rise in temperature. It *does* result in an increase of internal energy, which include potential energy.)

### 13.4 The $TdS$ Equations

The three  $TdS$  equations have been known to generations of students as the “tedious equations” – though they are not at all tedious to a true lover of thermodynamics, because, among other things, they *enable us to calculate the change of entropy* during various reversible processes in terms of either  $dV$  and  $dT$ , or  $dP$  and  $dT$ , or  $dV$  and  $dP$ , and even in terms of directly measurable quantities such as the coefficient of expansion and the bulk modulus.

i.) We can express entropy in terms of any two of  $PVT$ . Let us first express entropy as a function of  $V$  and  $T$

$$dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT. \quad 13.4.1$$

Therefore

$$TdS = T \left( \frac{\partial S}{\partial V} \right)_T dV + T \left( \frac{\partial S}{\partial T} \right)_V dT. \quad 13.4.2$$

From a Maxwell relation (equation 12.6.15),  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ . Also, in a constant volume process,  $TdS = dU$  so that  $T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V$ .

Therefore 
$$TdS = T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT. \quad 13.4.3$$

This is the first of the  $TdS$  equations.

ii.) This time, let us express entropy as a function of  $P$  and  $T$

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT. \quad 10.4.4$$

Therefore 
$$TdS = T\left(\frac{\partial S}{\partial P}\right)_T dP + T\left(\frac{\partial S}{\partial T}\right)_P dT. \quad 13.4.5$$

From a Maxwell relation (equation 12.6.16),  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ . Also, in a constant pressure process,  $TdS = dH$  so that  $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = C_P$ .

Therefore 
$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT. \quad 13.4.6$$

This is the second of the  $TdS$  equations.

iii.) If we express entropy as a function of  $P$  and  $V$  (recall that we can choose to express a function of state as a function of any two of  $P$ ,  $V$  or  $T$ ) we have

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV. \quad 13.4.7$$

Therefore 
$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV. \quad 13.4.8$$

In a constant volume process,  $TdS = C_V dT$ , so that  $T\left(\frac{\partial S}{\partial P}\right)_V = C_V \left(\frac{\partial T}{\partial P}\right)_V$ .

And in a constant pressure process,  $TdS = C_p dT$ , so that  $T\left(\frac{\partial S}{\partial V}\right)_P = C_p\left(\frac{\partial T}{\partial V}\right)_P$ .

Therefore 
$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV. \quad 13.4.9$$

This is the third of the  $TdS$  equations.

In summary, then, these are the three  $TdS$  equations:

$$TdS = T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT. \quad 13.4.3$$

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT. \quad 13.4.6$$

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV. \quad 13.4.9$$

These equations can be used, for example, to calculate, by integration, the change of entropy between one state and another, provided that the equation of state is known in order that we can evaluate the partial derivatives.

### 13.5 Expansion, Compression and the $TdS$ Equations

It will be recalled, from equations 13.3.1 and 13.1.8, that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} \quad \text{and} \quad \left(\frac{\partial V}{\partial T}\right)_P = \beta V. \quad 13.5.1a,b$$

That is, 
$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{\kappa}{\beta} \quad \text{and} \quad \left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\beta V}. \quad 13.5.2a,b$$

With these, the  $TdS$  equations become

$$dS = \frac{\beta}{\kappa} dV + \frac{C_V}{T} dT, \quad 13.5.3$$

$$dS = -\beta V dP + \frac{C_P}{T} dT \quad 13.5.4$$

and

$$dS = \frac{C_V \kappa}{T \beta} dP + \frac{C_P}{T \beta V} dV. \quad 13.5.5$$

These equations can be used, for example, to calculate, by integration, the change of entropy between one state and another, provided that  $\beta$ ,  $\kappa$  and the heat capacities are known as functions of temperature and pressure or specific volume. You don't even have to know the equation of state.

They won't tell us anything about an *ideal gas* that we don't already know, but let's just apply them to an ideal gas in any case, just to see if we have made any mistakes so far. For an ideal gas, as we saw in Sections 13.1 and 13.2,  $\beta = 1/T$  and  $\kappa = 1/P$ . The first two  $TdS$  equations become

$$TdS = PdV + C_V dT \quad 13.5.6$$

and

$$TdS = -VdP + C_P dT. \quad 13.5.7$$

That is to say,

$$TdS = PdV + dU \quad 13.5.8$$

and

$$TdS = -VdP + dH \quad 13.5.9$$

so all is well with the world so far. The third equation becomes

$$dS = C_V \frac{dP}{P} + C_P \frac{dV}{V}. \quad 13.5.10$$

For a reversible adiabatic process,  $dS = 0$ , so what do you get if you integrate equation 13.5.10 for a reversible adiabatic process for an ideal gas? This should complete your happiness – though there is more to come.

If a material (be it solid, liquid or gas) is compressed reversibly and *adiabatically* (i.e.  $dS = 0$ ), equation 13.5.3 **will tell you how the temperature changes with volume**:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\beta T}{\kappa C_V}. \quad 13.5.11$$

If it is the pressure, rather than the volume, that is changed reversibly and *adiabatically*, equation 13.5.4 **will tell you how the temperature changes with pressure:**

$$\left(\frac{\partial T}{\partial P}\right)_S = +\frac{\beta VT}{C_P}. \quad 13.5.12$$

In equation 13.5.11,  $\kappa$  is the isothermal compressibility, defined in equation 13.2.1 as

$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ . To emphasize that this is the *isothermal* compressibility, I'll add a

subscript:  $\kappa_{\text{iso}}$ . There is also a need to define an *adiabatic* compressibility,

$\kappa_{\text{ad}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ . (Note - I used the word *adiabatic*, but I used the subscript *S* to the

partial derivative. Are the words *adiabatic* and *isentropic* synonymous?) This is going to be less than the isothermal compressibility, because, if you try to compress a material adiabatically it will become hot and therefore not be as readily compressible as if the compression were isothermal. Now refer to equation 13.5.5,

$dS = \frac{C_V \kappa_{\text{iso}}}{T\beta} dP + \frac{C_P}{T\beta V} dV$ . For a reversible adiabatic process,  $dS = 0$ , so that

$\frac{C_V \kappa_{\text{iso}}}{T\beta} dP = -\frac{C_P}{T\beta V} dV$ . Divide both sides by  $dP$  and go to the infinitesimal limit,

recalling that in a reversible adiabatic process  $S$  is constant, and this equation then gives

us  $C_V \kappa_{\text{iso}} = -C_P \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ . But  $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$  is the adiabatic compressibility, and

$C_P / C_V = \gamma$ , so we arrive at

$$\frac{\kappa_{\text{iso}}}{\kappa_{\text{ad}}} = \gamma, \quad 13.5.13$$

where  $\gamma$  is the ratio of the isobaric and isochoric heat capacities. In particular, recall that, for an ideal gas,  $\kappa_{\text{iso}} = 1/P$ . Hence, for an ideal gas,  $\kappa_{\text{ad}} = 1/(\gamma P)$ .

In equation 13.3.2, we deduced the relation  $C_P - C_V = \frac{TV\beta^2}{\kappa_{\text{iso}}}$ . In equation 13.5.13, we

have deduced an expression for the ratio of the isothermal to adiabatic compressibilities, the isothermal compressibility being greater. Combining these now with  $\gamma = C_P / C_V$ , we can now deduce an expression for the *difference* between the isothermal and adiabatic compressibilities, namely:

$$\kappa_{\text{iso}} - \kappa_{\text{ad}} = \frac{TV\beta^2}{C_p}. \quad 13.5.14$$

In terms of *bulk modulus*  $B$ , which is the reciprocal of compressibility, equations 13.5.13 and 13.5.14 are, of course,  $\frac{B_{\text{ad}}}{B_{\text{iso}}} = \gamma$  and  $\frac{1}{B_{\text{iso}}} - \frac{1}{B_{\text{ad}}} = \frac{TV\beta^2}{C_p}$ .

Comparison of equations 13.3.2 and 13.5.14 shows that

$$\frac{C_p}{C_v} = \frac{\kappa_{\text{iso}}}{\kappa_{\text{ad}}}. \quad 13.5.15$$

Sir Isaac Newton in his *Principia* correctly deduced that the speed of sound in a gas is equal to  $\sqrt{1/(\rho\kappa)}$ , where  $\rho$  is the density, and without making any distinction between  $\kappa_{\text{iso}}$  and  $\kappa_{\text{ad}}$ . The measured speed was faster than predicted from his theory, and Newton tried, not completely successfully, to account for the difference. I haven't gone into the history, but there is a story – probably apocryphal – that, in order to secure agreement between observation and theory, he “fudged his lab” and “adjusted” his experimental results a little. But the trouble was not with the experimental results. If you take for  $\kappa$  the isothermal value, namely  $1/P$  for an ideal gas (to which air approximates quite well over the small pressure changes involved), the theory gives  $\sqrt{P/\rho}$  for the sound speed. In fact, however, the compressions and rarefactions in a sound wave are so rapid that they are, in effect, adiabatic, so that it is the adiabatic compressibility  $\kappa_{\text{ad}}$  that should be used, giving  $\sqrt{\gamma P/\rho}$  as the theoretical expression, which agrees well with the observed speed.

### 13.6 *Young's Modulus*

This Section is under revision.

### 13.7 *Bulk and Rigidity (Shear) Moduli*

When we are discussing the *bulk modulus* of a material we are usually thinking in terms of applying pressure and noting the compression, so the adiabatic bulk modulus is usually greater than the isothermal bulk modulus. We could in principle also imagine a situation in which we are moving a material into a vacuum, thus decreasing the external pressure, and then measuring the resulting expansion. In that case we would find that the adiabatic bulk modulus is less than the isothermal bulk modulus – but that is a rather artificial situation. In Section 13.5 we derived (see equation 13.5.14) the usual relation for compression:

$$\frac{1}{B_{\text{iso}}} - \frac{1}{B_{\text{ad}}} = \frac{\beta^2 T}{\rho C_p}, \quad 13.7.1$$

in which  $\beta$  is the volume coefficient of expansion, and  $C_p$  is the specific heat capacity at constant pressure. (Compare this with equations 13.6.12 and 13.6.20.)

We now must ask ourselves what is the difference between the adiabatic and isothermal rigidity moduli (also known as shear modulus). If you are unfamiliar with the rigidity modulus, see my Classical Mechanics notes, Chapter 20, Section 20.3.

The rigidity modulus involves no change in volume or length, and hence *there is no difference between the adiabatic and isothermal rigidity moduli.*

### 13.8 Volume, Temperature and the Grüneisen Parameter

If you compress a material adiabatically and reversibly (i.e. isentropically) its temperature goes up. The amount by which it goes up can be represented by the partial derivative  $\left(\frac{\partial T}{\partial V}\right)_S$ . Here,  $V$  could mean the total volume, the specific volume or the molar volume, according to context, and you would have to specify your units accordingly. The derivative is negative, because the temperature goes up as the volume is decreased.

[Compare this with the definition of the volume coefficient of expansion  $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ , which is positive. Think about the difference.]

A dimensionless version which also expresses the variation of temperature with volume would be  $\frac{V}{T} \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial \ln T}{\partial \ln V}\right)_S$ , and here there is no need to specify whether  $V$  means

total, specific or molar. The derivative could also be written as  $-\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S$ , where  $\rho$  is

the density. The positive value,  $-\left(\frac{\partial \ln T}{\partial \ln V}\right)_S = +\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S$  is called the *Grüneisen*

*parameter*. We have already used the symbols  $G$ ,  $g$ ,  $\Gamma$  and  $\gamma$  for various things in these notes, so I am stuck for a suitable symbol. Sometimes non-italic symbols are used for dimensionless parameters, such as  $R$  for Reynolds number in aerodynamics. Let's try  $Gr$  for the Grüneisen parameter.

For an *ideal gas*, the relation between volume and temperature in a reversible adiabatic expansion is  $TV^{\gamma-1} = \text{constant}$ , and therefore the Grüneisen parameter for an ideal gas is  $\gamma - 1$ .

In thinking about volume and temperature changes, we often have some sort of a gas (ideal or otherwise) in mind. However, geophysicists have to deal with very large pressures in the interior of the Earth, where volume and temperature changes of solids under pressure are not negligible, and geophysicists often make use of the Grüneisen parameter for solid materials.

For a bit of practice in deriving relationships between some of the quantities described in this chapter, see if you can show that

$$\text{Gr} = \frac{\beta}{\rho C_V \kappa_{\text{iso}}} = \frac{\beta}{\rho C_P \kappa_{\text{ad}}} \quad 13.8.1$$

and

$$\gamma = 1 + \text{Gr} \beta T. \quad 13.8.2$$

If  $\rho$  in these questions stands for density (mass per unit volume), what, precisely, are  $C_V$  and  $C_P$ ? Total, specific or molar? Or does it not matter? What do these equations become in the case of an ideal gas?