

13.5: Expansion, Compression and the TdS Equations

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

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

That is,

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

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 β , κ 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, κ 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: κ_{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, $dS = \frac{C_V \kappa_{\text{iso}}}{T\beta} dP + \frac{C_P}{T\beta V} dV$. 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 $C_P/C_V = \gamma$, C_P/C_V so we arrive at

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

where γ 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 ρ is the density, and without making any distinction between κ_{iso} and κ_{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 κ 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 κ_{ad} that should be used, giving $\sqrt{\gamma P/\rho}$ as the theoretical expression, which agrees well with the observed speed.

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