

4.3: Compressibility and Expansivity

Isothermal Compressibility (κ_T)

A very important property of a substance is how compressible it is. Gases are very compressible, so when subjected to high pressures, their volumes decrease significantly (think Boyle's Law!) Solids and liquids however are not as compressible. However, they are not entirely incompressible! High pressure will lead to a decrease in volume, even if it is only slight. And, of course, different substances are more compressible than others.

To quantify just how compressible substances are, it is necessary to define the property. The **isothermal compressibility** is defined by the fractional differential change in volume due to a change in pressure.

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (4.3.1)$$

The negative sign is important in order to keep the value of κ_T positive, since an increase in pressure will lead to a decrease in volume. The $1/V$ term is needed to make the property intensive so that it can be tabulated in a useful manner.

Isobaric Thermal Expansivity (α)

Another very important property of a substance is how its volume will respond to changes in temperature. Again, gases respond profoundly to changes in temperature (think Charles' Law!) whereas solids and liquid will have more modest (but not negligible) responses to changes in temperature. (For example, If mercury or alcohol didn't expand with increasing temperature, we wouldn't be able to use those substances in thermometers.)

The definition of the **isobaric thermal expansivity** (or sometimes called the expansion coefficient) is

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (4.3.2)$$

As was the case with the compressibility factor, the $1/V$ term is needed to make the property intensive, and thus able to be tabulated in a useful fashion. In the case of expansion, volume tends to increase with increasing temperature, so the partial derivative is positive.

Deriving an Expression for a Partial Derivative (Type I): The reciprocal rule

Consider a system that is described by three variables, and for which one can write a mathematical constraint on the variables

$$F(x, y, z) = 0$$

Under these circumstances, one can specify the state of the system varying only two parameters independently because the third parameter will have a fixed value. As such one could define two functions: $z(x, y)$ and $y(x, z)$.

This allows one to write the total differentials for dz and dy as follows

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (4.3.3)$$

and

$$dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz \quad (4.3.4)$$

Substituting the Equation 4.3.4 expression into Equation 4.3.3:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x \left[\left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz \right] \quad (4.3.5)$$

$$= \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial z} \right)_x dz \quad (4.3.6)$$

If the system undergoes a change following a pathway where x is held constant ($dx = 0$), this expression simplifies to

$$dz = \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial z} \right)_x dz$$

And so for changes for which $dz \neq 0$,

$$\left(\frac{\partial z}{\partial y} \right)_x = \frac{1}{\left(\frac{\partial y}{\partial z} \right)_x}$$

This *reciprocal rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straightforward, albeit less rigorous, manner. Begin by writing the total differential for $z(x, y)$ (Equation 4.3.3):

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

Now, divide both sides by dz and constrain to constant x .

$$\frac{dz}{dz} \Big|_x = \left(\frac{\partial z}{\partial x} \right)_y \frac{dx}{dz} \Big|_x + \left(\frac{\partial z}{\partial y} \right)_x \frac{dy}{dz} \Big|_x \quad (4.3.7)$$

Noting that

$$\begin{aligned} \frac{dz}{dz} \Big|_x &= 1 \\ \frac{dx}{dz} \Big|_x &= 0 \end{aligned}$$

and

$$\frac{dy}{dz} \Big|_x = \left(\frac{\partial y}{\partial z} \right)_x$$

Equation 4.3.7 becomes

$$1 = \left(\frac{\partial z}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x$$

or

$$\left(\frac{\partial z}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial z} \right)_x}$$

This “formal” method of partial derivative manipulation is convenient and useful, although it is not mathematically rigorous. However, it does work for the kind of partial derivatives encountered in thermodynamics because the variables are **state variables** and the differentials are **exact**.

Deriving an Expression for a Partial Derivative (Type II): The Cyclic Permutation Rule

This alternative derivation follow the initial steps in the derivation above to Equation 4.3.6:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial z} \right)_x dz$$

If the system undergoes a change following a pathway where z is held constant ($dz = 0$), this expression simplifies to

$$0 = \left(\frac{\partial z}{\partial x} \right)_y dy + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z dx$$

And so for and changes in which $dx \neq 0$

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This *cyclic permutation rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straight-forward, albeit less rigorous, manner. As with the derivation above, we begin by writing the total differential of $z(x, y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dx and constrain to constant z .

$$\left.\frac{dz}{dx}\right|_z = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dx}\right|_z + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dx}\right|_z \quad (4.3.8)$$

Note that

$$\left.\frac{dz}{dx}\right|_z = 0$$

$$\left.\frac{dx}{dx}\right|_z = 1$$

and

$$\left.\frac{dy}{dx}\right|_z = \left(\frac{\partial y}{\partial x}\right)_z$$

Equation 4.3.8 becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

which is easily rearranged to

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This type of transformation is very convenient, and will be used often in the manipulation of partial derivatives in thermodynamics.

✓ Example 4.3.1: Expanding Thermodynamic Functions

Derive an expression for

$$\frac{\alpha}{\kappa_T} \quad (4.3.9)$$

in terms of derivatives of thermodynamic functions using the definitions in Equations 4.3.1 and 4.3.2.

Solution

Substituting Equations 4.3.1 and 4.3.2 into the Equation 4.3.9

$$\frac{\alpha}{\kappa_T} = \frac{\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p}{-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T}$$

Simplifying (canceling the $1/V$ terms and using transformation Type I to invert the partial derivative in the denominator) yields

$$\frac{\alpha}{\kappa_T} = - \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T$$

Applying Transformation Type II give the final result:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T} \right)_V$$

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