

4.2: Total and Exact Differentials

The fact that we can define the *constant volume heat capacity* as

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V \quad (4.2.1)$$

suggests that the internal energy depends very intimately on two variables: volume and temperature. In fact, we will see that for a single component system, state variables are always determined when two state variables are defined. In the case of internal energy, we might write $U = f(V, T)$ or $U(V, T)$.

This suggests that the way to change U is to change either V or T (or both!) And if there is a mathematical function that relates the internal energy to these two variables, it should be easy to see how it changes when either (or both!) are changed. This can be written as a **total differential**:

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT \quad (4.2.2)$$

Even without knowing the actual mathematical function relating the variables to the property, we can imagine how to calculate changes in the property from this expression.

$$\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V} \right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T} \right)_V dT$$

In words, this implies that we can think of a change in U occurring due to an *isothermal change* followed by an *isochoric change*. And all we need to know is the slope of the surface in each pathway direction. There are a couple of very important experiments people have done to explore the measurement of those kinds of slopes. Understanding them, it turns out, depends on two very important physical properties of substances.

Exact Differentials

We have seen that the total differential of $U(V, T)$ can be expressed as Equation 4.2.2. In general, if a differential can be expressed as

$$df(x, y) = P dx + Q dy$$

the differential will be an **exact differential** if it follows the **Euler relation**

$$\left(\frac{\partial P}{\partial y} \right)_x = \left(\frac{\partial Q}{\partial x} \right)_y \quad (4.2.3)$$

In order to illustrate this concept, consider $p(V, T)$ using the ideal gas law.

$$p = \frac{RT}{V}$$

The total differential of p can be written

$$dp = \left(-\frac{RT}{V^2} \right) dV + \left(\frac{R}{V} \right) dT \quad (4.2.4)$$

✓ Example 4.2.1: Euler Relation

Does Equation 4.2.4 follow the Euler relation (Equation 4.2.3)?

Solution

Let's confirm!

$$\left[\frac{1}{\partial T} \left(-\frac{RT}{V^2} \right) \right]_V \stackrel{?}{=} \left[\frac{1}{\partial V} \left(\frac{R}{V} \right) \right]_T$$
$$\left(-\frac{R}{V^2} \right) \checkmark \left(-\frac{R}{V^2} \right)$$

dp is, in fact, an exact differential.

The differentials of all of the **thermodynamic functions** that are **state functions** will be exact. Heat and work are not exact differential and dw and dq are called *inexact differentials* instead.

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