

3.1: Calculation of Internal Energy Changes

The internal energy (U) of a system is a thermodynamic state function defined as:

Definition: Internal Energy

Property of a system that can be either transferred or converted.

In the absence of chemical transformations, heat and work are the only two forms of energy that thermodynamics is concerned with. Keeping in mind [Definition: System-Centric](#), which gives the convention for the signs of heat and work, the internal energy of a system can be written as:

$$U = Q + W, \quad (3.1.1)$$

which we can write in differential form by considering that the internal energy is a state function, as:

$$dU = dQ + dW, \quad (3.1.2)$$

which, using [eq. 2.4.4](#) becomes:

$$dU = dQ - PdV. \quad (3.1.3)$$

Internal energy in isothermal processes

To study the behavior of the internal energy in a process at constant temperature ($dT = 0$), James Prescott Joule (1818–1889) created the apparatus depicted in Figure 3.1.1.

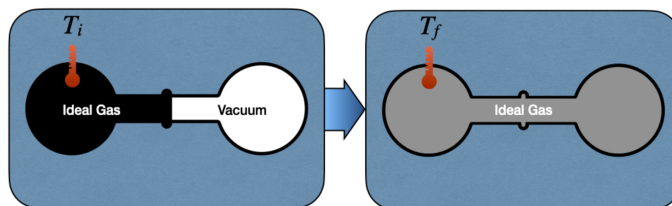


Figure 3.1.1: The Joule Expansion Experiment.

The left side of the Joule apparatus's inner chamber is filled with an ideal gas, while a vacuum is created in the right chamber. Both chambers are immersed in a water bath, to guarantee isolation from the environment. When the communication channel between the chambers is open, the gas expands and equilibrates. The work associated with the transformation is:

$$dW = -P_{\text{ext}}dV = 0, \quad (3.1.4)$$

since the chambers are not in communication with the environment, $P_{\text{ext}} = 0$. Thus, changes in internal energy are associated with the heat transfer of the process, which can be measured by monitoring the temperature of the gas at the beginning, T_i , and at the end of the experiment T_f . Joule noticed experimentally that if he used an ideal gas for this experiment, the temperature would not change $T_i = T_f$. Since the temperature doesn't change, there is no heat transfer, and therefore the internal energy stays constant:

$$dU = dQ = 0. \quad (3.1.5)$$

Note

Notice that Joule's conclusion is valid only for an ideal gas. If we expand a real gas, we do notice a change in temperature associated with the expansion. A typical example of this behavior is when you use a pressurized spray bottle and release its content for an extended time in the air. The container will typically get colder. We will discuss this behavior in [chapter 11](#) when we will study non-ideal gases.

From this simple experiment, we can conclude that the internal energy of an ideal gas depends only on its temperature.

Internal energy in adiabatic processes

An adiabatic process is defined as a process that happens without the exchange of heat. As such, $dQ = 0$, and the work associated with an adiabatic process becomes a state function:

$$dU = dW = -PdV, \quad (3.1.6)$$

which can then be calculated using the formulas that we derived in [section 2.4](#). Notice that isothermal and adiabatic are two very different processes. While an adiabatic process happens without the exchange of heat across the system's boundaries, this does not mean that the system's temperature does not change. Isothermal processes are usually associated with a heat transfer across the boundaries to maintain the temperature of the system constant. For adiabatic processes, it is quite the opposite since they are usually associated with a change in temperature.

Internal energy in isochoric processes

An isochoric process is a process in which the volume does not change. Therefore, $dW = 0$, and $dU = dQ_V$, which using [Equation 2.3.1](#), becomes:

$$dU = dQ_V = nC_V dT. \quad (3.1.7)$$

Since no work is performed at these conditions, the heat becomes a state function. Equation [3.1.7](#) also gives a mathematical justification of the concept of heat capacity at constant volume. C_V can now be interpreted as the partial derivative (a coefficient) of a state function (the internal energy):

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,n=1}, \quad (3.1.8)$$

where we have replaced the total derivative d with a partial one ∂ , and we have specified that the derivation happens at constant volume and number of moles. Equation [3.1.8](#) equation brings a rigorous definition of heat capacity at constant volume for 1 mol of substance:



Definition: Heat Capacity

The heat capacity of a substance, C_V , represents its ability to absorb energy at constant volume.

Internal energy in isobaric processes

In an isobaric process, the pressure does not change, hence $dP = 0$. Unfortunately, Equation [3.1.2](#) for this case does not simplify further, as happened in the two previous cases. However, in [section 2.3](#), we have introduced the useful concept of heat capacity at constant P . C_P was used in an adiabatic process in the same manner as C_V was used in the isochoric case. That is, as a coefficient to measure the amount of heat absorbed at constant pressure. Equation [3.1.8](#) gave a mathematical definition of C_V as the partial derivative of a state function (the internal energy). But if heat capacities are coefficients, and coefficients are partial derivatives of state functions, how do we explain C_P ? In order to do so, we can introduce a new state function, called the enthalpy (H), as:

$$H = U + PV, \quad (3.1.9)$$

and its differential, calculated as:

$$dH = dU + d(PV) = dU + PdV + \overbrace{VdP}^0, \quad (3.1.10)$$

which can be rearranged as:

$$dU = dH - PdV, \quad (3.1.11)$$

Replacing Equation [3.1.11](#) into Equation [3.1.3](#):

$$dH - PdV = dQ_P - PdV, \quad (3.1.12)$$

which simplifies to:

$$dH = dQ_P. \quad (3.1.13)$$

Equation 3.1.13 establishes that the heat exchanged at constant pressure is equal to a new state function called the enthalpy, defined by Equation 3.1.9. It also establishes a mathematical justification of the concept of heat capacity at constant pressure. Similarly to C_V , C_P can now be interpreted as the partial derivative (a coefficient) of the new state function (the enthalpy):

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P, n=1}, \quad (3.1.14)$$

Equation 3.1.14 brings also a rigorous definition of heat capacity at constant pressure for 1 mol of substance:

**Definition: Heat Capacity**

The heat capacity of a substance, C_P , represents its ability to absorb enthalpy at constant pressure.

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