

59-240 Introductory Physical Chemistry I - Supplementary Notes - Lecture 6

Additional Thoughts on the First Law

Why is it that internal energy (U) can be thought of as a state function and written as an exact differential, while this is not the case for work (w) and heat (q)? Let us first consider two examples:

Example 1: Calculate the work done if 2.00 mol of a perfect gas, which initially occupies a volume of 30.0 L at 280 K, is allowed to expand reversibly and isothermally to a total volume of 50.0 L.

Solution: note the following: p is not mentioned; $\Delta T = 0$ (isothermal), $p = p_{\text{ext}}$ (reversible expansion). Since this is a perfect gas undergoing reversible expansion,

$$p_{\text{gas}} = \frac{nRT}{V} = p_{\text{ext}} = p_{\text{opp}}$$

The internal pressure, p_{int} , equals the pressure of the gas, p_{gas} , and the pressure that opposes the expansion (say from atmospheric pressure), p_{opp} is called the external pressure, p_{ext} . We know

$$w = -\int_{V_1}^{V_2} p_{\text{opp}} dV$$

for reversible expansion. Thus, we can write:

$$\begin{aligned} w &= -\int_{V_1}^{V_2} p_{\text{gas}} dV = -\int_{V_1}^{V_2} \left(\frac{nRT}{V} \right) dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} \\ w &= -(2.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(280 \text{ K}) \left(\ln \frac{50.0}{30.0} \right) = -2.38 \text{ kJ} \end{aligned}$$

Example 2:

Calculate the work done in a non-reversible expansion for the perfect gas above under a constant pressure of 0.920 atm. Compare the final result to that in Example 1.

In this case, the equations are slightly different:

$$\begin{aligned} w &= -\int_{V_1}^{V_2} p_{\text{opp}} dV = -\int_{V_1}^{V_2} p_{\text{ext}} dV \\ &= -0.920 \text{ atm} \int_{30}^{50} dV = -0.920(50 - 30) \text{ atm} \\ &= -18.4 \text{ L atm} = (-18.4 \text{ L atm})(101.3 \text{ J L}^{-1} \text{ atm}^{-1}) = -1.86 \text{ kJ} \end{aligned}$$

Comparison: More work is obtained from the reversible process; in fact, -2.38 kJ is the maximum work possible under these circumstances.

State functions and exact differentials

Here, we show that a function corresponding to our definition of internal energy (in the notes and Atkins) must exist. The differential of a state function is an exact differential. A differential is exact if and only if the following conditions are satisfied:

1. The **line integral** is independent of path - the actual change in value equals the integral of differential change.
2. The **cyclic integral** equals zero - if the system returns to the original state, it has completed a cycle, and the value of the state function returns to the original value.
3. A function exists which can be differentiated to give the differential.

In the above examples, it was observed that work was done along two different paths between the same initial and final states. Since $\int dw$ is dependent upon the path, it is not an exact differential. This means that no function can be differentiated to yield dw , and $\oint dw \neq 0$.

From examples that you will attempt in the book, the same conclusions can be arrived at regarding heat. Thus, both dq and dw are defined as **inexact differentials**. One type of notation for this is to use the symbol \bar{d} (i.e., any sort of d with a stroke through it). So,

$$\oint \bar{d}w \neq 0 \quad \oint \bar{d}q \neq 0$$

In a cyclic process, $\Delta U = 0$. Then, according to the first law of thermodynamics, if work is done by the system, then an equivalent amount of heat must be added to the system ($w = -q$). For infinitesimally small changes then,

$$\oint \bar{d}w = -\oint \bar{d}q \quad \text{or} \quad \oint \bar{d}w + \oint \bar{d}q = 0 \quad \text{or} \quad \oint (\bar{d}w + \bar{d}q) = 0$$

Since the cyclic integral of the quantity in the parentheses equals zero, then this quantity **must be** an exact differential! If we can write $\oint dL = 0$, where $dL = \bar{d}w + \bar{d}q$, then the function L must be a state function. We dub this function the **internal energy**, and give it the symbol U , so that its total differential is written as:

$$dU = \bar{d}w + \bar{d}q$$

(which is another way of stating the first law of thermodynamics).

-RWS, September 29, 2005