**Heat, Work and Energy**

Thermodynamics asserts that the energy of a closed system increases if (i) heat $q$ flows from the surroundings into a system and (ii) the surroundings does work $w$ on the system [1].

$$\Delta U = q + w \quad (a)$$

Separation of the heat term from the work term is extremely important in the context of the Second Law of Thermodynamics. Heat flows spontaneously from high to low temperatures, the word ‘spontaneous’ being absolutely crucial in the context of the Second Law.

There are many ways in which the surroundings can do work on a system. At this stage we note the distinction which is drawn between the three variables $U$, $q$ and $w$. [The point is emphasised by use of upper and lower case letters.] The variables $q$ and $w$ describe pathways which can result in a change in thermodynamic energy. We make the point by rewriting equation (a) to show the change in thermodynamic energy on going from state I to state II.

Thus,

$$\Delta U = U(II) - U(I) = q + w \quad (b)$$

If for example $\Delta U = 100 \, \text{J}$, this can be a consequence of many pathways between state I and state II: e.g.

(a) $q = 50 \, \text{J}$, $w = 50 \, \text{J}$, (b) $q = 0 \, \text{J}$, $w = 100 \, \text{J}$ and (c) $q = 150 \, \text{J}$, $w = -50 \, \text{J}$.

Hence $U$ is a function of state (or, state variable) although $q$ and $w$ are not state variables. This is a triumph of the First Law of Thermodynamics.

The task faced by chemists is to identify and describe quantitatively the actual pathway accompanying, for example, a given chemical reaction.

Equation (a) signals the energy difference $\Delta U$ between two states which might involve a comparison of the energies at the start and finish of a chemical reaction in a closed system. In developing our argument there is merit in considering the change in energy of the original system following a small change along the overall reaction pathway.

We consider a closed reaction vessel containing ethyl ethanoate (aq; 0.1 mol) and NaOH(aq; excess) . Spontaneous chemical reaction leads to
hydrolysis of the ester to form EtOH(aq). The change in thermodynamic energy $\Delta U$ equals $U(II) - U(I)$. We subdivide the total chemical reaction into small steps where the change in composition, (i.e. $d\xi$) is accompanied by a change in thermodynamic energy $dU$.

$$\Delta U = \int_{\text{state I}}^{\text{state II}} dU$$  \hspace{1cm} (c)

If the volume of the system changes by the differential amount $dV$ such that the pressure within the closed system equals the confining pressure $p$ [2],

$$w = -p \cdot dV$$  \hspace{1cm} (d)

Then [3],

$$dU = q - p \cdot dV$$  \hspace{1cm} (e)

We write equation (e) in the following form;

$$q = dU + p \cdot dV$$  \hspace{1cm} (f)

The right hand side of equation (f) contains the differential changes in two extensive state variables, $U$ and $V$. Consequently heat $q$ is precisely defined by the changes in thermodynamic energy and volume at pressure $p$.

**Footnotes**

[1] The ‘equivalence‘ of heat and work was first demonstrated in many experiments carried out in the 19th Century by James Joule, the son of a brewer (Salford, England). Joule showed that by doing work on a thermally isolated system the temperature of the latter increases. In other words, doing work on a system is equivalent to passing heat into the system.

The SI unit of energy is the joule, symbol J; $J \equiv kg \cdot m^2 \cdot s^{-2}$

Sometimes one reads that thermodynamics is not concerned with ‘time’. However the concept of energy and the unit of energy involves ‘time’. Of course the origins of these concepts are classical mechanics and accompanying discussion of potential and kinetic energies.

[2] $p \cdot V = [N \cdot m^{-2}] \cdot [m^3] = [N \cdot m] = [J]$

[3] The fundamental link between heat and work was established by Joule. Interestingly the link between heat and work was apparent
previously to A. Haller who suggested that human bodies are heated by
the friction between solid particles in the blood passing through the
capillaries in the lungs; see comments by
(b) M. A. Paul, Principles of Chemical Thermodynamics, McGraw-Hill,
New York, 1957, p52.