Thermochimica Acta, 10 (1974) 1-5

AN APPROACH TO THERMODYNAMICS

J. A. POULIS
Department of Physics, University of Technology, Eindhoven (The Netherlands)
(Received 4 March 1974)

ABSTRACT

Suggestions are given for a new method of teaching thermodynamics starting from a minimum knowledge of quantum mechanics. For didactical reasons much reference is made to systems having only two energy levels in order to minimise difficulties in understanding the concepts of equilibrium and non-equilibrium.

INTRODUCTION

One of the greatest problems in teaching thermochemistry is the treatment of fundamental thermodynamics. Recently this problem has become more serious as the oil crisis has initiated many discussions about other energy sources. Since in these discussions many people take part who are not specialised in chemistry or physics, they frequently have to go to thermochemists for information on the laws of thermodynamics.

In the present paper the author gives an outline of a method of treatment of thermodynamics which starts from quantum statistics in so simple a form that secondary school education will suffice for the understanding.

As the treatment starts from Bohr's model of quantum mechanics, application of the results is, strictly speaking, restricted to systems of independent particles. In comparison with the usual fundamental treatment we therefore have a loss of generality.

HEAT

As said above we start with Bohr's equation

$$E_2 - E_1 = hf \tag{1}$$

We suppose the student to be acquainted with the meaning of energy levels and the frequency (f) of the electromagnetic radiation which occurs when a molecule falls from the higher level (E_2) to the lower one (E_1).

At this point it is useful to explain that emission of radiation is a special kind of heat emission and that heat emission by conduction also involves that a molecule passes to a lower energy level. At the same time it may be pointed out that a molecule receiving heat through conduction or through absorption of radiation passes to a higher energy level.

In general: the passing of a molecule from one energy level to another is always accompanied by a heat flow to or from the molecule, taking into account the conservation of energy, which in mathematical form, reads

$$\sum_i E_i \delta N_i = \mathrm{d}Q \tag{2}$$

where N_i stands for the occupation of the level E_i.

EXTERNAL WORK

For the understanding of the following it is necessary to take another small side-step to quantum mechanics and consider the fact that the energy levels postulated by Bohr can be calculated with Schrödinger's equation once the potential energy versus position curve is known. This potential energy curve can be calculated from the external forces acting on the particle.

When the external forces are submitted to variations, the potential energy curve, and with it the height of the energy levels, will vary. Let us consider a molecule in a given energy level and let us assume that owing to some external influence, the height of this energy level decreases. This means that our molecule loses energy, it delivers external work (A) to the external forces.

This reads:

$$\sum_i N_i \delta E_i = -\mathrm{d}A \tag{3}$$

INTERNAL ENERGY

We define the internal energy U as the sum of the energies of all the particles of our system

$$\sum_i N_i E_i = U \tag{4}$$

FIRST LAW OF THERMODYNAMICS

Differentiating eqn (4) we obtain:

$$\mathrm{d}(\sum N_i E_i) = \sum E_i \mathrm{d}N_i + \sum N_i \mathrm{d}E_i \tag{5}$$

Using eqns (2) and (3), this equation reads

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}A \tag{6}$$

which is the familiar version of the first law of thermodynamics.

ENTROPY

To define the entropy, we make a difference between two ways of describing the situation of a system of particles. In both cases we start from a given arrangement of the energy levels.

In the global description we only give the numbers N_i of molecules occupying the levels. Actually, so far we have used this global description in this paper. In the detailed description we also say which molecules are in which level.

One single global description will correspond to a number of different detailed ones. This number we shall call W.

At this stage we have to make use of simple statistical reasoning in that we use:

$$W = \frac{N!}{N_1!\,N_2!\ldots} \tag{7}$$

The entropy of the system described in the global way can now be defined as

$$S = k \log W = k \log \frac{N!}{N_1!\,N_2!\ldots} \tag{8}$$

where k stands for Boltzmann's constant.

TEMPERATURE

A particular difficulty in thermodynamics is the introduction of the concept of equilibrium.

The trouble is that for the definition of equilibrium one needs the use of quantities, the definition of which requires knowledge of the concept of equilibrium. In our treatment this vicious circle can be avoided by restricting ourselves for some time to a very special kind of systems, viz., those which have only two energy levels. (Such systems are familiar to people working in the field of magnetism.)

We can define the temperature T by:

$$\frac{N_1}{N_2} = e^{-\frac{E_1 - E_2}{kT}} \tag{9}$$

For two-level systems this definition is unambiguous and does not require special restriction to equilibrium conditions. Another way of expressing the last statement is by saying that two-level systems are always in internal equilibrium.

SECOND LAW OF THERMODYNAMICS FOR SYSTEMS IN EQUILIBRIUM

We now consider the situation in which we apply the amount of heat given by

$$\Delta Q = E_1 - E_2$$

to our two-level (equilibrium) system. This implies that one molecule will be able to jump from the second to the first level. It therefore follows that

$$\Delta N_1 = -\Delta N_2 = 1 \tag{10}$$

and

$$\Delta S = k \log \frac{N!}{(N_1+1)!(N_2-1)!} - k \log \frac{N!}{N_1!\,N_2!} = k \log \frac{N_2}{N_1+1} \tag{11}$$

When restricting ourselves to large values of N_1 and N_2 it follows with the help of eqn (9) that

$$\Delta S = k \log \frac{N_2}{N_1} = \frac{E_1-E_2}{kT} = \frac{\Delta Q}{T} \tag{12}$$

This final result is known as the second law of thermodynamics for systems in equilibrium.

SECOND LAW OF THERMODYNAMICS FOR SYSTEMS NOT IN EQUILIBRIUM

The easiest way to make our considerations applicable to non-equilibrium situations is to start from two separate systems A and B each characterised by two energy levels, so each being in internal equilibrium.

The energy differences between the two levels are taken to be equal in both systems. We suppose that the two systems cannot exchange particles but this heat transport does not exist (adiabatic situations). For a global description of the two systems together one has to know the values of the occupations: $N_{A_1} N_{A_2} N_{B_1}$ and N_{B_2}.

According to simple statistical reasoning given by the number W of detailed descriptions corresponding to a single global situation:

$$W = \frac{N_A!\,N_B!}{N_{A_1}!\,N_{A_2}!\,N_{B_1}!\,N_{B_2}!} \tag{13}$$

We define the entropy as

$$S = k \log W = k \log \frac{N_A!}{N_{A_1}!\,N_{A_2}!} + k \log \frac{N_B!}{N_{B_1}!\,N_{B_2}!} \tag{14}$$

We now consider a small variation in the situation caused by an energy quantum transported from the A system to the B system. So $\Delta N_{A_2} = -\Delta N_{A_1} = \Delta N_{B_1} = -\Delta N_{B_2} = 1$. This will cause a variation of the entropy given by

$$\Delta S = -k \log \frac{N_{A_2}+1}{N_{A_1}} + k \log \frac{N_{B_2}}{N_{B_1}+1} = \left(\frac{1}{T_B} - \frac{1}{T_A}\right)(E_1 - E_2) \tag{15}$$

If we now link the spontaneity of the situation variation with the growth of the number W, i.e., with positive values of ΔS, we learn from eqn (15) that the heat transportation from the A system to the B system will take place spontaneously when $T_A > T_B$. This is in accordance with one of the usual conceptions of the second law of thermodynamics: In an isolated system heat flow will only occur from high to low temperatures.