

17 Chemical equilibrium

Subject:

“In a chemical process, chemical equilibrium is the state in which the chemical activities or concentrations of the reactants and products have no net change over time. Usually, this state results when the forward chemical reactions proceed at the same rate as their reverse reactions. The rates of the forward and reverse reactions are generally not zero but, being equal, there are no net changes in any of the reactant or product concentrations. This process is known as dynamic equilibrium.”

Deficiencies:

Consider two subsystems A and B. There are several types of equilibrium, namely as many as there are extensive variables X , which can be exchanged between A and B. (Only the energy does not define its own equilibrium, since it is exchanged together with any of the other extensive quantities.) To each of the extensive quantities X belongs an “energy-conjugated” intensive quantity ξ . If the systems A and B can exchange the extensive quantity X , this exchange comes to a halt only when the corresponding intensive variable has the same value for A and B, i.e. when $\xi_A = \xi_B$. Now the two subsystems are in equilibrium with regard to the exchange of X . The various equilibria are named according to the exchanged quantity. If two systems can exchange entropy, they are in “thermal equilibrium” when their temperatures are equal, i.e. when $T_A = T_B$. Two Systems that can exchange electric charge are in the state of “electric equilibrium” when their electric potentials are equal, i.e. when $\phi_A = \phi_B$. Two bodies which exchange momentum in a frictional process do so until their velocities have become equal, i.e. until there is “velocity equilibrium”, or $v_A = v_B$. If in a chemical reaction the amounts of the substances A(1), A(2), A(3), ... can change at the expense of the amounts B(1), B(2), B(3), ..., the substances at the one side of the reaction equation are in “chemical equilibrium” with those of the other side, when the sum of the chemical potentials of the substances A(i) equals the sum of the potentials of substances B(k), i.e. when $\sum \mu_{A(i)} = \sum \mu_{B(k)}$.

When placing the chemical equilibrium in a broader framework, as we just have done, it is seen that it is not appropriate to emphasize that the chemical equilibrium is a *dynamic* equilibrium.

Consider again, for comparison, the electric equilibrium, and, to be concrete a piece of copper wire. Now imagine the wire consisting of two halves A and B. Sure enough they are in a state of electric equilibrium. It is common and reasonable to say that there is no electric current flowing between these two subsystems. If however, we describe this state in the same way as chemistry describes the chemical equilibrium, we would not be allowed to say that there is no current, since there is a continuous movement of electrons from A to B and from B to A, that results for a copper wire with a cross section of 1 mm² in an electric current of 10⁸ A in one direction and a current of the same intensity in the other direction. Correspondingly, when no wind is blowing we would not be allowed to say that the air is at rest but we should say that we have a mass flow of about 100 kg/(m² · s) to the right and a similar flow to the left, and also currents of the same intensity back

and forth and upwards and downwards. Similar conclusions would be drawn for thermal equilibrium, where we have currents of phonons in all directions, or for the velocity equilibrium related to continuous flows of momentum in opposite directions.

Of course, there is nothing incorrect in considering a phenomenon at the microscopic level. But, first, there is no essential difference in this respect between chemical equilibrium and other equilibria, for which nobody emphasizes that the equilibrium is a “dynamic equilibrium”. And second, one is stressing something that easily leads to a misconception. If we say that in a copper wire in which no net current is flowing, “in reality” there are two counter-flowing currents, should the wire not heat up? Correspondingly, one could ask, why the two counter-running chemical reactions are not dissipative? Obviously, these problems are home-made. One is intermixing the arguments of two levels of description, the microscopic and the macroscopic.

Origin:

The description of chemical reactions on the simple, phenomenological level by means of the chemical potential has never won recognition. This is different from the other, physical phenomena mentioned above. There it is understood to describe a heat transport as caused by a temperature difference or an electric current by an electric potential gradient. The microscopic interpretation of these processes is done later in the context of atomic and solid state physics. Chemistry begins right from the beginning at the molecular level, on which the simple and elegant thermodynamical quantities need a complicated interpretation.

Disposal:

Say that, when chemical equilibrium is reached, the reaction has come to a halt. This does not hinder us to consider the continuous forth and back reaction at a later advanced state. Just as we say that in the state of electric equilibrium we say that no electric current is flowing, and that this does not hinder us, to explain this state later on microscopically by the symmetry of the Fermi surface.

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