

## 2.3.2: The Principle of Detailed Balance

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The principle of **detailed balance** is formulated for kinetic systems which are decomposed into elementary processes (collisions, or steps, or elementary reactions): *At equilibrium, each elementary process should be equilibrated by its reverse process.* Lewis put forward this general principle in 1925:

*Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process.*<sup>[1]</sup>

According to Ter Haar,<sup>[2]</sup> the essence of the detailed balance is:

*...at equilibrium the number of processes destroying situation A and creating situation B will be equal to the number of processes producing A and destroying B*

The principle of detailed balance was explicitly introduced for collisions by Ludwig Boltzmann. In 1872, he proved his H-theorem using this principle. The arguments in favor of this property are founded upon microscopic reversibility. In 1901, R. Wegscheider introduced the principle of detailed balance for chemical kinetics. In particular, he demonstrated that the irreversible cycles



are impossible and found explicitly the relations between kinetic constants that follow from the principle of detailed balance. This system is more accurately described thusly:



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