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NEGATIVE TEMPERATURE STATES IN CHEMICAL REACTIONS

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Using the alkali-halide reactions as an example we show that chemical reactions proceeding via excited electronic states can result in the formation of a state with negative temperature. Estimates show that chain reactions are the most useful if this effect is to be used for maser action. Any metastable state excited as a result of the chemical reaction favors the formation of a negative temperature state.

In a number of chemical reactions the individual reactants combine in the molecule via an excited electronic state.[1] If a negative temperature state is to be produced the number of excited particles appearing as products of the reaction must exceed the number of such particles in the unexcited state. If there are no reaction products present in the initial state, then to produce a negative temperature state it is necessary and sufficient that

$$k^+/g_+ > k^-/g_-, \tag{1}$$

where k^+ is the specific rate of the reaction that proceeds via the formation of excited electronic states in the reaction products, k^- is the specific reaction rate that proceeds via the production of nonexcited reaction products, and $g_\pm$ is the statistical weight of a given state.

It is well known[1] that the reaction

$$\mathrm{Na_2 + Cl = NaCl + Na} \tag{2}$$

results in the appearance of excited Na atoms and the appearance of the yellow luminescence line (D-line) characteristic of Na. It has been shown experimentally[2] that at low pressures (10^{-3} mm Hg, where there is no collisional quenching of the luminescence) 80% of the Na atoms produced in the reaction radiate. Consequently

$$k^+/(k^+ + k^-) = 0.8. \tag{3}$$

The ratio of the statistical weights $g_+/g_- = 3$ and it follows from (3) that the condition in (1) is satisfied.

The fact that (1) is satisfied only means that negative temperature states are present at the initial time. In order to analyze the production of negative temperatures under steady-state conditions we consider the simple kinetic equations that describe the time dependence of the number of particles in various states

$$\begin{aligned} dn_+/dt &= C^+ - w_\mathrm{d} n_+ - W^+ n_+, \\ dn_-/dt &= C^- + w_\mathrm{d} n_+ - W^- n_-. \end{aligned} \tag{4}$$

Here n_+ and n_- represent the numbers of excited and nonexcited reaction products, C^+ and C^- are the reaction rates, w_d is the probability of radiative decay of the excited state, W^+ and W^- are the probabilities for removal of reaction products from the system.

In the stationary state $dn_+/dt = dn_-/dt = 0$ and the criterion for the formation of a negative temperature state $n_+/g_+ > n_-/g_-$ leads to the inequality

$$\frac{g_-}{g_+} > \frac{w_\mathrm{d}}{W^-} \frac{C^- + C^+}{C^+} + \frac{W^+}{W^-} \frac{C^-}{C^+}. \tag{5}$$

If $W^+ \lesssim W^-$ and if C^+ and C^- satisfy (1), then to satisfy (5) the quantity w_d/W^- must be small.

If the excited state resulting from the reaction is not metastable then $w_\mathrm{d} \approx 10^8\ \mathrm{sec^{-1}}$ and W^- must be of the order of $10^9\ \mathrm{sec^{-1}}$ or greater. It is difficult to provide this rate of removal of unexcited particles by usual pumping methods. It would be better to use absorption or to exploit a chemical reaction in which products are formed that do not exhibit spectral lines coinciding with the radiation lines. In particular, a reaction of this kind is exemplified by chain reactions of the Na-Cl type which, according to [1], proceeds via the scheme

$$\mathrm{Na_2 + Cl = NaCl + Na}, \qquad \mathrm{Na + Cl_2 = NaCl + Cl}. \tag{6}$$

For this kind of reaction the relation in (5) becomes

$$\frac{g_-}{g_+} > \frac{w_\mathrm{d}}{kX} \frac{k^+ + k^-}{k^+} + \frac{k^-}{k^+} \frac{k^*}{k}, \tag{7}$$

where X is the concentration of Cl_2, k and k* are the reaction rates for the processes $Na + Cl_2 = NaCl + Cl$ and $Na^* + Cl_2 = NaCl + Cl$ (Na^* is the excited sodium atom). For the D-line we have $w_d = 6 \times 10^7\ sec^{-1}$ while $k = 6 \times 10^{14}\ cm^3\ mole^{-1}\ sec^{-1}$ [2] so that a pressure of the order of an atmosphere would be needed to satisfy (7). It should also be noted that vapor of the alkali metals contains free electrons; this represents an added complication in the problem of obtaining negative states.

According to the relation in (6) the reaction Cs + Cl may be more favorable because $k^- \approx 0$ in this reaction.

If the reaction results in the formation of atoms in a metastable state "inoperative" atoms can be removed from the system by rapid pumping. A reaction of this type is exemplified by the thermal dissociation of CO_2 and N_2O, the ground state of which is $^1\Sigma$. Since the ground state of oxygen is ^3P, one expects that oxygen will be formed in the excited ^1D state in the dissociation process [1,3]

$$CO_2 \rightarrow CO\,(^1\Sigma) + O, \quad N_2O \rightarrow N_2\,(^1\Sigma) + O \qquad (8)$$

The ^1D state is metastable since it is a singlet while the ^3P ground state is a triplet. A pumping rate of 1000 liters/sec is completely adequate for removing the reaction products from a volume of 1 cm^3 in 10^{-6} sec. A disadvantage of the reaction in (8) is the need for heating the initial materials to high temperatures.

Attention is directed to the fact that many biochemical reactions occur via excited electronic states. [4] Hence, it is very possible that negative temperatures play an important role in biological processes.

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[1] Glasstone, Laidler, and Eyring, Theory of Rate Processes, (Russ. Transl. IIL, 1948).

[2] J. Magee, J. Chem. Soc. 8, 638 (1940).

[3] K. Laidler, Chemical Kinetics, Oxford, 1955.

[4] S. Reed, Excited Electronic States in Chemistry and Biology, (Russ. Transl.), 1960.

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