azimuthal quantum number, have been used to determine the theoretical values of S_2 and $C_{298\cdot 1}$ and the results compared with experimental values.

3. In the absence of further evidence, the best values for S_2 and $C_{298\cdot 1}$ are 64.92 and 104.57, respectively. (Entropy in calories, temperature in degrees centigrade absolute, pressure in atmospheres, molecular weight in grams per mole, moment of inertia in gram cm. squared per mole.)

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 31]

THE TEMPERATURE COEFFICIENT OF PHOTOCHEMICAL REACTION RATE

BY RICHARD C. TOLMAN

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I. Introduction

Let us consider a photochemical reaction, aA + bB + . . . ⟶ Products, taking place at some given temperature T, under the influence of radiation from an external source, the frequency of the radiation being ν, and its energy density throughout the reacting mixture being u_ν. If we confine our attention to cases where the rate of reaction is proportional to the energy density u_ν and where the law of Guldberg and Waage is followed, we may write for the rate of the above reaction the expression,

$$-\frac{dC_A}{dt} = k_\nu u_\nu C_A^a C_B^b \dots \tag{1}$$

The quantity k_ν occurring in Equation 1 may be called the *specific photochemical reaction rate*. It is the rate at which the reaction would proceed if the reacting substances were present at *unit concentration* and subjected to radiant energy of frequency ν and *unit energy density*. The quantity k_ν is a parameter, independent of the concentration and energy density, but dependent on the temperature T and frequency ν. The temperature T is to be taken as that which would exist if the illumination from the external source were cut off. It is the purpose of the following article to present a theoretical treatment of the change in k_ν with T.

In an earlier article,[1] the writer has already shown that for a *monomolecular* photochemical reaction, the temperature coefficient of photochemical reaction rate will be given by the equation

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2} \tag{2}$$

where $\bar{\bar{\epsilon}}$ is the average energy of the molecules which pick up radiant energy and react, $\bar{\epsilon}$ is the average energy of all the molecules and k is Boltzmann's constant. In the article referred to, the above equation

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[1] Tolman, THIS JOURNAL, **42**, 2506 (1920).

was obtained as a result which was incidental to a treatment of thermal reaction rates, and the methods employed were those of the classical statistical mechanics.

In this article we shall present a simple and direct proof of Equation 2, using the methods of the quantum theory instead of those of the classical statistical mechanics. Consideration will also be given to the temperature coefficient of *bimolecular* reactions, attention will be paid to the nature of the quantity $\frac{\partial}{\partial\nu}\left(\frac{\partial \ln k_\nu}{\partial T}\right)$, an interpretation of existing data on photochemical temperature coefficients will be given, a criticism will be made of Plotnikow's attempted classification of photochemical temperature coefficients into three groups, and some discussion of Einstein's law of photochemical equivalence will be presented.

We may now proceed to our theoretical treatment.

II. The Number of Molecules in a Given Quantum State

The chance that a molecule will pick up radiant energy and hence undergo a monomolecular change, or in the case of bimolecular reactions arrive in an activated state such as to facilitate reaction upon collision, will evidently depend not only upon the frequency and density of the radiant energy involved but also upon the internal condition or quantum state of the molecule at the time it is subjected to the radiant energy.

For the number of molecules N_i in the i^{th} quantum state we shall use the expression

$$N_i = N\frac{p_i e^{-\epsilon_i/kT}}{\sum\limits_0^\infty p_i e^{-\epsilon_i/kT}} \tag{3}$$

where N is the total number of molecules present, p_i is the a-priori probability that a molecule will be in the i^{th} quantum state, ϵ_i is the energy corresponding to the i^{th} quantum state, k and T have their usual significance and the summation $\sum\limits_0^\infty$ is to be carried out over all possible quantum states of the kind in question.

The justification for this equation rests at the present time largely upon its correspondence with the Maxwell-Boltzmann distribution law, familiar in the classical statistical mechanics, which may be written in the form

$$dN = N\frac{e^{-\epsilon/kT}d\sigma}{\int e^{-\epsilon/kT}d\sigma} \tag{4}$$

where ϵ is the energy of a molecule whose coördinates and momenta have values falling in the region $d\sigma$ and the integration $\int$ is to be taken over the whole of the generalized space σ. Equation 4 may be regarded as the limit approached by Equation 3 in the regions of generalized space corresponding to high quantum numbers where the successive energy levels are near together, the a-priori probabilities p_i occurring in Equation 3 and the size of the infinitesimal regions $d\sigma$ occurring in (4) being chosen so as to secure correspondence between (3) and (4) at the limit, thus satisfying the Bohr correspondence principle. The simplest procedure is to choose the a-priori probabilities as equal to the number of ways[2] in which a given quantum state can occur, and then adjust the size of $d\sigma$ so as to secure the desired correspondence.

III. Rate of a Monomolecular Photochemical Reaction

We may now proceed directly to obtain an expression for the rate of a monomolecular photochemical reaction. The mechanism of such a reaction may be pictured as consisting in the absorption of a quantum of radiant energy of magnitude $h\nu$ which raises the molecule to such an energy level that the monomolecular change can take place.

Let $\alpha_{i\nu}$ be the chance in unit time that a molecule in the i^{th} quantum state surrounded by radiant energy of frequency ν and unit density will absorb a quantum of energy $h\nu$, and $s_{i\nu}$ be the chance that such an activated molecule will undergo the monomolecular transformation in question. The quantity $s_{i\nu}$ will be unity only in case every activated molecule reacts without losing its activation before reaction by re-emission. Making use of Equation 3 for the number of molecules in the i^{th} quantum state we may then evidently write for the rate at which molecules are reacting under the influence of radiant energy of frequency ν and density u_ν the expression,

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = u_\nu N \frac{\sum\limits_0^\infty \alpha_{i\nu} s_{i\nu} p_i e^{-\epsilon_i/kT}}{\sum\limits_0^\infty p_i e^{-\epsilon_i/kT}} \tag{5}$$

where the summation $\sum\limits_0^\infty$ is to be taken over all possible states. Noting that $(-\mathrm{d}N/\mathrm{d}t)/(u_\nu N)$ is the quantity which we have called the specific photochemical reaction rate k_ν, we may now write,

$$k_\nu = \frac{\sum\limits_0^\infty \alpha_{i\nu} s_{i\nu} p_i e^{-\epsilon_i/kT}}{\sum\limits_0^\infty p_i e^{-\epsilon_i/kT}} \tag{6}$$

The above expression for photochemical reaction rate would permit a relatively complete solution of the whole problem of monomolecular photochemical reaction rate if we had sufficient knowledge of the values of $\alpha_{i\nu}$, $s_{i\nu}$, p_i and ϵ_i. At the present stage of scientific development, however, such knowledge is largely lacking. Moreover, at the present time we

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[2] For example, in the case of a rotating molecule of the dumb-bell model this would mean the number of possible distinguishable orientations having the same azimuthal quantum number, as determined from the theory of quantization in space.

have little knowledge of the absolute values of k_ν since few photochemical experiments have been made with *monochromatic* light of *known intensity.* For both these reasons we shall find it advisable to turn our main attention to the percentage temperature coefficient of k_ν rather than its absolute value, since the theoretical treatment of the temperature coefficient does away for the most part with the necessity of detailed knowledge of the quantities in Equation 6, and there is furthermore a considerable body of data on photochemical temperature coefficients.

IV. Temperature Coefficient of Monomolecular Photochemical Reaction Rate

Assuming the quantities $\alpha_{i\nu}$, $s_{i\nu}$ and p_i independent of the temperature, which is certainly justifiable as a first approximation, we may carry out a logarithmic differentiation of Equation 6 and obtain

$$\frac{\partial\, ln\, k_\nu}{\partial T} = \frac{1}{k_\nu}\frac{\partial k_r}{\partial T} = \frac{1}{k_\nu}\,\frac{\sum\limits_0^\infty \alpha_{i\nu}\, s_{i\nu}\, p_i\, e^{-\epsilon_i/kT}\,\frac{\epsilon_i}{kT^2}}{\sum\limits_0^\infty p_i\, e^{-\epsilon_i/kT}} - \frac{\sum\limits_0^\infty p_i\, e^{-\epsilon_i/kT}\,\frac{\epsilon_i}{kT^2}}{\sum\limits_0^\infty p_i\, e^{-\epsilon_i/kT}}\cdot$$

An examination of the first term on the right hand side of the above equation will show that it is equal to the average energy before activation of the molecules which actually pick up radiant energy and react, divided by kT^2. The second term is obviously the average energy of all the molecules divided by kT^2. Hence we may rewrite the above equation in the form

$$\frac{\partial\, ln\, k_\nu}{\partial T} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2} \tag{7}$$

where the symbols $\bar{\bar{\epsilon}}$ and $\bar{\epsilon}$ have the significance explained above.[3]

Before proceeding to a consideration of the interpretation of experimental facts with the help of this very simple equation, we shall first show that a slightly modified form of Equation 7 will also apply to dimolecular reactions.

V. Rate of a Bimolecular Photochemical Reaction

The mechanism of a bimolecular photochemical reaction may be pictured as consisting in the activation of one or both of the molecules entering into the reaction followed by collision and reaction. Let the reaction in question be A + B $\longrightarrow$ Products and let us consider the case in which only the molecules of A are activated by the extraneous radiation. For

[3] The similarity of this equation in form to that for thermal reactions should be noted. In the case of thermal reactions, however, the quantity $\bar{\bar{\epsilon}} - \bar{\epsilon}$ must be replaced by the whole energy of activation. See Tolman, Ref. 1.

the number of such activated molecules $N_{i\nu}$ present at any given time with the energy

$$\epsilon_{i\nu} = \epsilon_i + h\nu \tag{8}$$

we may evidently write

$$N_{i\nu} = N_{\mathrm{A}} \frac{u_\nu \, \alpha_{i\nu} \, \tau_{i\nu} \, p_i \, e^{-\epsilon_i/kT}}{\sum\limits_0^\infty p_i \, e^{-\epsilon_i/kT}} \tag{9}$$

where N_{A} is the total number of molecules of A, $\alpha_{i\nu}$ is the chance per unit time that a molecule in the i^{th} quantum state will pick up a quantum when surrounded by unit energy density of frequency ν, and $\tau_{i\nu}$ is the average life that such an activated molecule exists without reëmission. Furthermore, for the number of molecules of B in the j^{th} quantum state we may write,[4]

$$N_j = N_{\mathrm{B}} \frac{p_j \, e^{-\epsilon_j/kT}}{\sum\limits_0^\infty p_j \, e^{-\epsilon_j/kT}} \tag{10}$$

The chance that a molecule of A in the quantum state $i\nu$ will collide with a molecule of B in the quantum state j will evidently be proportional to the product of the concentrations of molecules in these states, and in the case of gases as a first approximation to the square root of the absolute temperature. Hence if we denote by $s_{i\nu j}$ the chance that reaction will take place on a collision between molecules in these states, we may evidently write with the help of Equations 9 and 10 for the rate of the dimolecular reaction the expression,

$$-\frac{1}{v}\frac{\mathrm{d}N_{\mathrm{A}}}{\mathrm{d}T} = k_c T^{1/2} \frac{N_{\mathrm{A}}}{v} \frac{N_{\mathrm{B}}}{v} u_\nu \frac{\sum\limits_0^\infty \sum\limits_0^\infty \alpha_{i\nu} \, \tau_{i\nu} \, s_{i\nu j} \, p_i \, e^{-\epsilon_i/kT} \, p_j \, e^{-\epsilon_j/kT}}{\left(\sum\limits_0^\infty p_i \, e^{-\epsilon_i/kT}\right)\left(\sum\limits_0^\infty p_j \, e^{-\epsilon_j/kT}\right)}$$

where v is the volume of the container, k_c is a constant which determines the number of collisions when the temperature is given, and the summation in the numerator is to be taken over all states i and j. If we again define k_ν as the rate of reaction at unit concentrations under the influence of unit energy density we may write

$$k_\nu = k_c T^{1/2} \frac{\sum\limits_0^\infty \sum\limits_0^\infty \alpha_{i\nu} \, \tau_{i\nu} \, s_{i\nu j} \, p_i \, e^{-\epsilon_i/kT} \, p_j \, e^{-\epsilon_j/kT}}{\left(\sum\limits_0^\infty p_i \, e^{-\epsilon_i/kT}\right)\left(\sum\limits_0^\infty p_j \, e^{-\epsilon_j/kT}\right)} \tag{11}$$

As in the case of monomolecular reactions, we shall find it more informing to consider the temperature coefficient of reaction rate rather than its absolute value and shall proceed to obtain its value.

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[4] In obtaining Formulas 9 and 10 we assume that the values of $N_{i\nu}$ and $N_{j\nu}$ are not appreciably affected by losses through reaction.

VI. Temperature Coefficient of Bimolecular Photochemical Reaction Rate

Carrying out a logarithmic differentiation of Equation 11 we obtain

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{1}{k_\nu}\frac{\partial k_\nu}{\partial T} = \frac{1}{2T} + \frac{1}{k_\nu} k_c T^{1/2} \frac{\sum\limits_0^\infty \sum\limits_0^\infty \alpha_{i\nu}\tau_{i\nu} s_{i\nu j} p_i e^{-\epsilon_i/kT} \frac{\epsilon_i}{kT^2} p_j e^{-\epsilon_j/kT}}{\left(\sum\limits_0^\infty p_i e^{-\epsilon_i/kT}\right)\left(\sum\limits_0^\infty p_j e^{-\epsilon_j/kT}\right)}$$

$$+ \frac{1}{k_\nu} k_c T^{1/2} \frac{\sum\limits_0^\infty \sum\limits_0^\infty \alpha_{i\nu}\tau_{i\nu} s_{ij\nu} p_i e^{-\epsilon_j/kT} p_j e^{-\epsilon_j/kT} \frac{\epsilon_j}{kT^2}}{\left(\sum\limits_0^\infty p_i e^{-\epsilon_i/kT}\right)\left(\sum\limits_0^\infty p_j e^{-\epsilon_j/kT}\right)}$$

$$- \frac{\sum\limits_0^\infty p_i e^{-\epsilon_i/kT} \frac{\epsilon_i}{kT^2}}{\sum\limits_0^\infty p_i e^{-\epsilon_i/kT}} - \frac{\sum\limits_0^\infty p_j e^{-\epsilon_j/kT} \frac{\epsilon_j}{kT^2}}{\sum\limits_0^\infty p_j e^{-\epsilon_j/kT}}$$

An examination of the terms in the above equation shows that it may be rewritten in the form

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{1}{2T} + \frac{\bar{\bar{\epsilon}}_A + \bar{\bar{\epsilon}}_B - \bar{\epsilon}_A - \bar{\epsilon}_B}{kT^2}, \qquad (12)$$

where $\bar{\bar{\epsilon}}_A$ is the average energy before activation of the molecules of A which pick up radiant energy and then react, $\bar{\bar{\epsilon}}_B$ is the average energy of the molecules of B which enter into the reaction and $\bar{\epsilon}_A$ and $\bar{\epsilon}_B$ are the average energies of all the molecules present. If it is desired, Equation 12 can be rewritten in the form

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{1}{2T} + \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2} \qquad (12a)$$

where $\bar{\bar{\epsilon}}$ is the average energy of the pairs of molecules of A and B that actually enter into the photochemical reaction and $\bar{\epsilon}$ is the average energy of any pair of molecules of A and B. Except for the negligible term $1/(2T)$ Equation 12a has the same form as Equation 7 for monomolecular reactions. It should be noted that the term $1/(2T)$ arises from the assumption that the number of collisions of the molecules of the gas is proportional to the square root of the absolute temperature. In the case of reactions taking place in a liquid medium, the decrease in the viscosity of the liquid with rise of temperature might be accompanied by a considerable increase in the chance of collision, so that a larger but probably roughly calculable term would have to be introduced.

Equations 12 and 12a were derived for a bimolecular reaction in which only one of the reacting substances was activated by the radiant energy in question. In case activation of both substances were involved the rate of reaction would no longer be proportional simply to the first power of the energy density and a somewhat more complicated treatment is necessary which is hardly worth considering at the present stage of experimental knowledge. Even in the case of a polymerization such as that of anthracene, it is not probable that both anthracene molecules are activated in an appreciable fraction of the collisions which lead to reaction, while in the case of reactions between unlike molecules one of the components is very often photo-active in the region of the spectrum used and the other inactive.

No treatment will be given at the present time of reactions of higher order than the second, since higher order collisions are of very improbable occurrence, and total changes of higher order than the second probably take place in many cases as the result of a series of changes of lower order.

VII. The Quantity $\frac{\partial}{\partial \nu}\left(\frac{\partial \ln k_\nu}{\partial T}\right)$

Before proceeding to an interpretation of experimental data let us consider the change in temperature coefficient with frequency. It is evident that the differentiation of either of the equations, 7 or 12a, for the two cases we have treated will lead to the same result, namely,

$$\frac{\partial}{\partial \nu}\left(\frac{\partial \ln k_\nu}{\partial T}\right) = \frac{1}{kT^2}\frac{\delta \bar{\epsilon}}{\delta \nu} \tag{13}$$

VIII. Relation between Two Methods of Expressing Temperature Coefficients

Temperature coefficients for rate of reaction are unfortunately usually expressed as the ratio r between the rates of reaction at temperatures separated by an interval of 10°C., in accordance with the expression

$$r = \frac{k_{T+10}}{k_T} \tag{14}$$

Expressing temperature coefficients in the more rational way adopted in this article, it is evident that we may write as a rough approximation

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{k_{T+10}-k_T}{10\,(k_{T+10}+k_T)/2} = \frac{r-1}{5(r+1)} \tag{15}$$

We may now proceed to the interpretation of existing experimental data.

IX. Interpretation of Experimental Values of Temperature Coefficients

The most striking fact concerning the temperature coefficients of photochemical reaction rates is the extremely great number of reactions for which the value of r is unity or only slightly greater than unity. Plotnikow,[5] in his admirable collection of existing information on photochemistry, lists 21 photochemical reactions for which the maximum value of r is 1.08.

The existence of such a group of reactions is readily understood on the basis of the developments presented in this article. The value unity for r means, in accordance with Equation 15, the value zero for $\partial \ln k_\nu/\partial T$.

[5] Plotnikow, "Lehrbuch der Photochemie," de Gruyter and Co., Berlin and Leipzig, 1920, p. 62.

Hence, in accordance with Equation 7 for monomolecular reactions, and also in accordance with Equation 12a for bimolecular reactions, provided we neglect the small term arising from increased frequency of collision, we may write

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2} = 0 \tag{16}$$

and may conclude that for this great group of well-known photochemical reactions the average energy of the molecules which enter into the reaction is practically the same as the average energy of all the molecules. This result is entirely understandable, since it merely means that the average molecule has as good a chance of picking up energy and becoming activated as the molecules in some special quantum state far removed in energy content from the average. For reactions of this group, preliminary partial activation of the molecule is not necessary in order that the molecule may absorb its quantum and react.

The above discussion also makes it clear that we ought to expect to find cases in which preliminary activation of the molecules *is* advantageous in promoting reaction. This may arise either because molecules in the lower quantum states are not in a condition to absorb radiant energy of the frequency used, or because the energy level which they attain after the absorption is not high enough to lead to chemical reaction. In such cases the average energy $\bar{\bar{\epsilon}}$ of the molecules which enter into the reaction will be greater than the average energy $\bar{\epsilon}$ of all the molecules and we shall find

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2} > 0, \quad \text{and} \quad r = \frac{k_{T+10}}{k_T} > 1 \tag{17}$$

As a matter of fact, Plotnikow[5] lists 17 reactions in which the ratio r varies from 1.17 to 1.50. Plotnikow believes that these reactions can be divided into two sub-groups having the approximate values for the ratio r of 1.20 and 1.40, and is also inclined to believe that the value 1.20 should be ascribed to the increase with temperature in the velocity of some diffusion process involved in the reaction, so that there would be only two true photochemical temperature coefficients, corresponding to $r = 1.00$ and $r = 1.40$.

On the basis of the theoretical developments presented in this article, there seems to be no ground for the point of view of Plotnikow. The most significant term in determining the value of the temperature coefficient will be $\bar{\bar{\epsilon}} - \bar{\epsilon}$ which is the difference between the average energy of the molecules which actually react and the average energy of all the molecules. This quantity will depend on the energy levels for the different quantized states of the particular substances involved and there is no reason why different substances should all have the same value of $\bar{\bar{\epsilon}} - \bar{\epsilon}$. The value zero for $\bar{\bar{\epsilon}} - \bar{\epsilon}$ is a very natural one to expect and this accounts for the large group of photochemical reactions with zero temperature coefficient, but there is no reason to suppose that when $\bar{\bar{\epsilon}}-\bar{\epsilon}$ is greater than zero it will be the same for different kinds of molecules as would be necessary to account for a unique value $r = 1.40$.

In the case of second order reactions, in addition to the effect of the term $\bar{\bar{\epsilon}}-\bar{\epsilon}$ in determining temperature coefficients, we shall also have to consider, as pointed out above, the effect of temperature in increasing the number of collisions between the reacting molecules. In gaseous systems the number of collisions will be roughly proportional to the square root of the absolute temperature and this will produce a negligible increase in reaction velocity with increasing temperature. In liquid systems the decrease in viscosity with rising temperature may be large enough to produce a measurable effect on reaction velocity. Similar considerations will apply to heterogeneous reactions where diffusion of the reacting substances to a catalytic surface is necessary for reaction. Since the viscosity of water at room temperature decreases about 20% for a 10° rise, this might account in some cases as suggested by Plotnikow for a value $r = 1.20$. It should be noted, however, that of the 7 reactions which Plotnikow lists as belonging to the group with the value 1.20, 3 are gaseous reactions, so that his explanation can hardly be a general one.

Further evidence as to the tenability of the theory of temperature coefficient here presented, is afforded by a calculation of the magnitude of $\bar{\bar{\epsilon}}-\bar{\epsilon}$. If in accordance with Equations 7 and 15 we write

$$\frac{\partial \ln k_v}{\partial T} = \frac{\bar{\bar{\epsilon}}-\bar{\epsilon}}{kT^2} = \frac{r-1}{5(r+1)},$$

and take $r = 1.40$ and $T = 300°$, as typical, we obtain for $\bar{\bar{\epsilon}}-\bar{\epsilon}$ the value 6000 cal. per mol. This corresponds to a value of 0.26 volts per molecule which is an entirely reasonable figure for the difference in energy contents between successive quantum levels in a molecule.

A monomolecular photochemical reaction taking place at room temperature in a homogeneous system with a temperature coefficient corresponding to $r = 1.40$ might be very reasonably interpreted by assuming that the molecules in the lowest quantum state were not photo-active, and that molecules had to be in the next highest quantum state with a preliminary activation corresponding to 0.26 volts in order to absorb light and react. The relative numbers of molecules in the first and second quantum states would be given in accordance with Equation 3 by the expression

$$\frac{N_1}{N_2} = \frac{p_1\, e^{-\epsilon_1/kT}}{p_2\, e^{-\epsilon_2/kT}}$$

Since the ratio of the a-priori probabilities p_1/p_2 is certainly small, we may temporarily take it as unity; substituting the value of $\bar{\bar{\epsilon}}-\bar{\epsilon}$ corresponding to 0.26 volts we then obtain for our particular case the ratio,

$N_1/N_2 = 22{,}000$. We thus see that practically all the molecules will be in the lowest quantum state[6] and that the difference, $\bar{\bar{\epsilon}}-\bar{\epsilon}$, between the average energy of the molecules which react and the average energy of all the molecules will be approximately, as assumed above, the difference between the energy levels in the lowest and next to the lowest quantum states. The process of reaction itself will consist in the picking up of a quantum $h\nu$ by molecules in the next to the lowest quantum state followed by reaction. If the photo-active light has the wave length $500\mu\mu$ this denotes a further increase in energy level corresponding to an activation of 2.5 volts per molecule, again an entirely reasonable figure.

Before leaving the subject of temperature coefficients, the question naturally arises whether negative temperature coefficients might be possible, owing to the fact that molecules in the lowest quantum state could pick up radiant energy of the frequency employed and molecules in the second quantum state not be able to do this. It will be seen from the above discussion, however, that at room temperature with probable values of the difference in energy between the first and second quantum states, nearly all the molecules in any case would be in the lowest quantum state, and negative temperature coefficients would not be probable since a lowering of the temperature would not appreciably increase the percentage of molecules in the lowest quantum state.

X. Interpretation of Experimental Values of $\frac{\partial}{\partial\nu}\left(\frac{\partial\, ln\, k_\nu}{\partial T}\right)$

In Section VII we showed that the change in temperature coefficient with frequency for a photochemical reaction is given by the equation

$$\frac{\partial}{\partial\nu}\left(\frac{\partial\, ln\, k_\nu}{\partial T}\right) = \frac{1}{kT^2}\frac{\partial\bar{\bar{\epsilon}}}{\partial\nu}$$

Since $\bar{\bar{\epsilon}}$ is the average energy of the molecules that actually react, this quantity may decrease with frequency, for at higher frequencies the magnitude of the quantum $h\nu$ is increased and molecules from a lower quantum state may be raised to a level where reaction is possible. This means that we may expect to find cases where the second derivative in question is negative, provided $(\partial\, ln\, k_\nu/\partial T)$ is not already zero.

Experimental data of the kind in question are not numerous nor certain. Nevertheless, referring once more to Plotnikow's treatise, we find that silver citrate paper has the temperature coefficient $r = 1.19$ in the blue and 1.07 in the ultraviolet; the phototropic substance salicylidene-β-

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[6] We exclude the possibility of an appreciable number of molecules in quantum states higher than the second owing to the still greater energy of these states, and the increased volume which would accompany the higher states. For the case of monatomic hydrogen, the distribution of atoms in the different quantum states, *allowing for the increased volume of the atom in the higher quantum states*, has been treated by Urey in an article which will probably appear in the *Astrophysical Journal.*

naphthylamine has the values 1.8 in the green, 1.45 in the blue and 1.39 in the violet; and the reaction between chlorine and hydrogen has the values 1.50 for green light (550–530$\mu\mu$), 1.31 for blue light (490–470$\mu\mu$) and 1.21 for violet light (400–350$\mu\mu$). These results if reliable are in complete agreement with the theory here presented.

XI. Remarks on Einstein's Law of Photochemical Equivalence

Although the main purpose of this article has been to consider the temperature coefficient of photochemical rate of reaction, a few words concerning Einstein's law of photochemical equivalence will not be out of place. According to this law the number of molecules that enter into a photochemical reaction should be equal to the number of quanta of radiant energy absorbed. It is evident from the discussion presented in this paper, however, that molecules may sometimes absorb a quantum of energy and then lose it by re-emission before reacting. This would be true in the case of monomolecular reactions unless the quantity $s_{i\nu}$ occurring in Equation 6 should be unity, and in the case of bimolecular reactions unless the product $r_{i\nu}\, s_{i\nu j}$ occurring in Equation 11 should be great enough to assure reaction for every molecule activated. Thus we should expect to find many reactions in which the actual amount of reaction falls below that predicted by an over simplified statement of Einstein's law, and this agrees with the experimental facts.[7] Cases might also occur in which the primary photochemical reaction is followed by secondary reactions which would make the total change greater than that predicted. This case apparently occurs under certain conditions in the reaction between hydrogen and chlorine and has been discussed by Nernst.[8] The situation may be summed up by stating that although Einstein's law of photochemical equivalence presumably holds for individual molecular changes it may not hold for the total end result of a photochemical reaction as macroscopically determined.

XII. Conclusion and Summary

1. A simple equation for the temperature coefficient of photochemical reaction rate has been derived on the basis of the quantum theory. The equation agrees with that previously obtained by the author[1] using the methods of the classical statistical mechanics.

2. Existing data on temperature coefficients of photochemical reactions have been successfully interpreted with the help of the equation. It has been shown that Plotnikow's division of photochemical temperature coefficients into three distinct classes is apparently not tenable.

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[7] For the best work in this field see Warburg's papers in the *Berichte der Berliner Akadamie.*

[8] Nernst, *Z. Elektrochem.*, **24**, 335 (1918).

3. An equation for change in temperature coefficient with frequency has been derived and successfully used in interpreting existing data.
4. The causes for apparent deviations from Einstein's law of photochemical equivalence have been discussed.
5. Experimental work in this Laboratory is now in progress for further testing the ideas presented in this article.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE ADSORPTION OF GASES BY COPPER

BY ROBERT N. PEASE[1]

RECEIVED JULY 11, 1923

During a recent investigation of the combination of ethylene and hydrogen in the presence of metallic copper,[2] a considerable amount of data on the adsorption isotherms of hydrogen, ethylene, ethane and carbon monoxide on copper was accumulated. As these results show many points of special interest, it has seemed worth while to devote a separate paper to them.

The apparatus, procedure and method of preparation of the copper and the gases have already been described[2] and need not be repeated here in detail. Suffice it to say that adsorptions at a series of pressures between 0 and 760 mm. were determined by admitting the gases in small quantities to an evacuated bulb containing the copper and measuring the pressure after equilibrium had been established. The dead space in the bulb and connecting tubes was determined by the use of helium, which was assumed not to be adsorbed.

The absorbent consisted of about 100 g. of copper granules prepared by reduction of copper oxide by hydrogen at 200° in its original position.

Adsorption Isotherms on Active Copper at 0°

The adsorption isotherms at 0° in the presence of active copper are shown graphically in Fig. 1. Ethane was not actually run on this sample but its comparative behavior is known from two other series on similar samples of copper. An isotherm has been sketched in for completeness. Nitrogen was also run on this sample but the variability of the results indicated the presence of varying but small quantities (less than 0.5%) of some strongly adsorbed impurity. The nitrogen was prepared from ammonium chloride and sodium nitrite and was purified by passage through sulfuric acid, phosphorus pentoxide and a tube cooled in a mixture of solid carbon dioxide

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[1] The work represented by this paper was performed while the author was National Research Fellow at Princeton University.

[2] Pease, THIS JOURNAL, 45, 1196 (1923).