UCRL-17313

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Submitted to the
Journal of Chemical Physics

UCRL-17313
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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December 1966

UCRL-17313

Some Thermodynamics of Photochemical Systems*

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A limit on the thermodynamic potential difference between the ground and excited states of any photochemical system is established by evaluating the potential difference at which the rate of photon absorption and emission are equal; the relationship of absorption and emission is given by a Planck law relationship between the two, provided that there is thermal equilibrium between the sublevels of each electronic band. The actual potential developed may be evaluated if the quantum yield of luminescence is known. The maximum amount of power storage obtainable is evaluated by lowering the potential difference until the product of the potential difference and the fraction of the quanta retained is maximized. The history and applications of the Planck law relation between absorption and emission spectra are discussed briefly, and applications of the potential difference calculation are mentioned.

I. INTRODUCTION

The purpose of this paper is to discuss the interaction of a radiation field with a photochemical system which absorbs radiation over a broad band of frequencies. Of primary concern are the evaluation of the chemical potential difference which is developed within the system, and the amount of work--or, equivalently, free-energy--which may appear as a result of light absorption by such a system.

The thermodynamics of the interaction of a narrow-band absorber with a radiation field,[1] and limitations on the amount of work which may be extracted by such an absorber from a radiation field,[2] are fairly well understood. In this paper we extend discussions of the narrow-band situation to apply them to broad-band systems. The thermodynamics of broad-band-absorbing photochemical systems has been considered in a more restricted context by Shockley and Queisser,[3] and we use a Planck blackbody law relationship between the absorption and emission properties of a broad-band absorber which has been derived by a number of authors (see Discussion).

We consider a two-level photochemical system which is comprised of a collection of ground electronic states G and excited electronic states E. Ordinarily these consist of the ground singlet states and the first excited singlet states of the light-absorbing molecules. In systems where excitations can migrate easily, these collections of states are often referred to as the valence band and the conduction band, respectively. Each electronic band usually contains a number of vibrational substates.

When the rate of absorption of light quanta causing excitations from G to E is rapid with respect to the thermal equilibration of populations between the two bands, then a transition from E to G gives up some free-energy which may be stored or used for chemical synthesis. The amount of work which can be done as a result of each photon absorbed is limited by the product of this free-energy change and the quantum yield for the deexcitation pathway which is coupled to work production.

If the substates within each electronic band remain in thermal equilibrium regardless of the incident radiation field, then the potential difference between any substate of G and any substate of E will be independent of the identity of either substate. In other words, there will be a single well-defined free-energy change for any transition between the bands.

There are two ways of viewing the excitations caused by the absorption of light: Excitations may be considered as producing an increase in the population of electrons in a set of states of fixed number, with a corresponding decrease in the population of electrons in another set of states of fixed number. Alternatively, the identical process may be viewed as an increase in the number of an excited state molecular species and a concomitant decrease in the number of a ground state molecular species.

These two points of view may be called the <u>photoelectric</u> and the <u>molecular photochemical</u> views, respectively, and the distinction between the two becomes meaningful when one considers the coupling between the light-absorbing molecules, and the larger system of which they are a part. If this system operates through electron migration,

then the photoelectric view is the more natural, while if the result of light-absorption is molecular rearrangement, then the molecular photochemical view may prevail.

It is important to remember that the distinction is one of point of view only, as influenced by the fate of the excitation, and makes no difference in the thermodynamics of the light-absorption.

The formalism for the photoelectric case has been extensively developed for use in semiconductor systems.[4,5] In the presence of complete thermal equilibrium, the chemical potential of all of the electrons is equal to the Fermi level, which usually lies midway in energy between the ground band and the excited state band. The electrons within the E band and within the G band each have a chemical potential which is similarly defined, and which is called a quasi-Fermi level. As electrons are transferred from G to E under the influence of light, the quasi-Fermi level of G drops below the equilibrium Fermi level, and the quasi-Fermi level of E increases correspondingly.

The alternative point of view is to consider changes in the partial molar free energy of the light-absorbing molecules in their ground state and in their excited state. The action of light usually depletes the population of the ground state molecules only very slightly, altering the chemical activity of these species to a negligible extent; in this case the potential difference arising between the bands is due almost entirely to the greatly increased population of molecules in the excited state.

II. THEORY

In order to evaluate the band-to-band potential difference μ caused by a radiation field in any given situation, we first consider the conditions for equilibrium between the band-to-band transitions and a radiation field. Reversible reaction implies that there is no change in entropy accompanying the emission or absorption of radiation by the photochemical system at any frequency.

The entropy change corresponding to the loss of a photon of frequency ν from a radiation field may be evaluated by considering an equilibrium at ν between the field and a blackbody: A blackbody is in equilibrium with a radiation field at ν when[6]

$$I(\nu) = (8\pi n^2\nu^2/c^2)\,[\exp(h\nu/kT_B) - 1]^{-1}, \tag{1}$$

where T_B is the temperature of the blackbody, n is the refractive index of the medium, and I is the intensity of the radiation field in units of photons per 4π solid angle, per unit bandwidth, per unit area, per unit time.

The entropy gained by a blackbody upon absorption of a photon at ν is $h\nu/T_B$. By rearranging (1) to find the temperature of a blackbody in equilibrium with a radiation field of intensity I, we find the entropy change upon loss of a photon from a radiation field to be

$$-\partial S/\partial N = k \ln(1 + 8\pi n^2\nu^2/c^2 I). \tag{2}$$

From the assumed potential difference μ and knowledge that the energy change per photon absorbed is $h\nu$, we know that the change in the entropy of the photochemical system per photon absorbed is

$$\partial S/\partial N = (h\nu - \mu)/T, \tag{3}$$

where T is the temperature of the surroundings.

If we assume that the photochemical absorber is isotropic in its interaction with a radiation field, then by integrating over solid angle, and equating the entropies, we find that the rate of photon absorption and emission per unit bandwidth and unit cross-section is

$$I(\nu,\mu,T) = 8\pi(n\nu/c)^2\{\exp[(h\nu-\mu)/kT]-1\}^{-1}. \qquad (4)$$

The figure one in (4) corresponds to stimulated emission, and may usually be neglected, simplifying (4) to

$$I(\nu,\mu,T) = 8\pi(n\nu/c)^2 \exp[(\mu-h\nu)/kT]. \qquad (4')$$

If the absorption cross-section for band-to-band excitation is $\sigma(\nu,\mu,T)$, then the total rate of excitation and emission per unit bandwidth is equal to

$$\sigma(\nu,\mu,T)I(\nu,\mu,T) \qquad (5)$$

for a photochemical system which has thermal equilibrium at temperature T within its electronic bands, and a potential difference μ between the bands, and which is in equilibrium with an isotropic radiation field at all frequencies.

Now consider that the same potential difference is established between the bands of the same system by any manner whatsoever. This might be done by causing the same rate of excitations with an arbitrary radiation field, or by pumping the system electrically or chemically. Since we are assuming rapid thermal equilibration among the vibrational substates within each band, the equilibrium radiation field may be replaced with anything else which will cause the same net rate of G-to-E transitions without affecting either the potential between the bands, or the quantity and frequency distribution of radiation spontaneously emitted by the system.

This means that, given thermal equilibrium within each band, knowledge of the electronic absorption spectrum of any system permits direct calculation of the luminescence spectrum, and vice versa. This relation has been derived in general and for specific cases by a number of independent authors. We discuss its history and applications in Section III.

This Planck law relationship between absorption and emission may be used to calculate the potential developed in a photochemical system whenever its absorption spectrum and the incident light flux are known. For simplicity we assume that the absorption spectrum is independent of μ, although this may not be true. Changes with temperature can be ignored since T is assumed to be fixed.

The rate of band-to-band excitations resulting from an arbitrary radiative field is equal to

$$R_{in} = \int \sigma(\nu) I_S(\nu) d\nu. \tag{6}$$

where $I_S(\nu)$ is the photon flux provided by the light source.

From (5), with (4') substituted in, the rate of radiative decay from a photochemical system having a potential difference μ is

$$R_{lum} = [\exp(\mu/kT)] \int 8\pi(n\nu/c)^2 \sigma(\nu) \exp(-h\nu/kT) d\nu. \tag{7}$$

We shall abbreviate the integral with L, so that

$$R_{lum} = e^{\mu/kT} L. \tag{7'}$$

By equating (6) and (7'), we can find the maximum possible potential of a photochemical system having an absorption spectrum $\sigma(\nu)$, and illuminated by a radiation field of intensity and distribution $I_S(\nu)$:

$$\mu_{max} = kT \ln(R_{in}/L). \tag{8}$$

Non-radiative band-to-band transitions are frequently a significant source of E-to-G relaxation. We assume that the rate of induced G-to-E transitions given by (6) is large with respect to all spontaneous excitations. Then we specify that the total rate of decay from E to G is κ times the rate of radiative decay alone:

$$R_{out} = \kappa(\mu) L e^{\mu/kT}. \tag{9}$$

By equating R_{in} and R_{out} we determine the potential developed in the presence of non-radiative relaxation:

$$\mu = kT \ln[R_{in}/\kappa(\mu)L] = \mu_{max} - kT \ln[\kappa(\mu)]. \tag{10}$$

As κ is the reciprocal of the luminescence quantum yield, it may frequently be determined experimentally. For the remainder of this section we assume that κ is independent of μ, although it appears that this is generally true only for non-interacting excitations obeying Boltzmann statistics.

Work is one of the more popular commodities which can result from the photochemical absorption of light, so that frequently one desires to maximize the amount of power stored by such a system.

The amount of power stored is

$$P = (R_{in} - R_{loss})\mu, \tag{11}$$

where R_{loss} is the rate of E-to-G transitions which are not coupled to the work storage process.

From (10) we know that

$$\mu_o = \mu_{max} - kT \ln(R_{loss}/R_{lum}) \tag{12}$$

is the potential difference in the absence of the work storage processes. We define the quantum yield for the loss processes

$$\phi_{loss} = R_{loss}/R_{out}, \tag{13}$$

so that

$$\mu = \mu_o + kT \ln \phi_{loss}. \tag{14}$$

The amount of power stored, which may be rewritten as

$$P = R_{in}\, \mu(1 - \phi_{loss}), \tag{15}$$

may be maximized by appropriate choice of μ and ϕ_{loss}. The power storage is approximately maximal when $\phi_{loss} = kT/\mu_o$, so that the optimal potential is roughly

$$\mu = \mu_o - kT \ln(\mu_o/kT). \tag{16}$$

This more general derivation is strictly parallel to the narrow-band treatment which was given previously.[2]

III. DISCUSSION

The Planck law relationship between absorption and emission was derived several decades ago by Kennard,[7,8] but this work has only recently been rediscovered.[9] The relationship was discovered independently by Stepanov,[10] and his derivation has been extended somewhat by Neporent[11] and by Ketskemety, Dombi, and Horvai.[12] The relationship was also derived, again independently, for a more restricted situation by van Roosbroeck and Shockley,[13] and their work has recently been generalized by McCumber.[14]

Until these several papers revived application of the relationship to all kinds of spectra, it appears that the direct connection between the relative strengths of absorption and emission as a function of frequency was used only in systems where individual vibrational or rotational lines could be resolved,[15] and in these applications the direct nature of the relationship between absorption and emission spectra has not been made explicit.

The experimental validity of the relationship was first shown by Kennard[7] and Merrit[16] for several species of dye molecule in solution, and following rediscovery of the relationship by Stepanov it has been used fairly extensively by Russian and Hungarian physical chemists. Work with a variety of molecules in solution has shown very good agreement between calculated and observed luminescence spectra;[12] indeed, the agreement is so good that discrepancies between theory and experiment have been used to determine the presence of impurities.[17] Some comparisons between predicted and observed luminescence spectra have also been made in semiconductors,[18,19] and the agreement is within the

accuracy of the measurements. The relationship has even been used successfully in the vapor phase,[20] demonstrating that vibrational equilibrium can be attained through intramolecular processes within the lifetime of the excited state.

The Planck law relation itself has a number of applications, some of which are suggested by the work which has already been done. One of the important applications is the use of an absorption spectrum to calculate a luminescence spectrum for systems in which luminescence has not been observed experimentally. Prediction of the luminescence spectrum may be useful in calculating energy transfer probabilities, and may assist in locating the luminescence experimentally. Examination of differences between predicted and observed luminescence spectra may provide a check on the experimental methods used, and represents a tool for examining deviations from the usual assumption of complete vibrational equilibrium in a two-level system.

Knowledge that the Planck law relationship is applicable, which seems assured for any two-level condensed system, permits a ready calculation of the maximum light-induced chemical potential difference which can be developed by a system, providing only that the incident light intensity and the absorption spectrum are known. Given knowledge of the quantum yield for luminescence, it is possible to calculate the actual potential developed. Knowledge of this potential may be useful in examining any photochemical system which uses light to generate any sort of thermodynamic potential gradient. We have found these calculations to be particularly useful in analyzing the energetics of photosynthesis.[21]

This process can also be reversed: From knowledge of a luminescence spectrum it is possible to infer the absorption spectrum of the species responsible. Then, given order-of-magnitude estimates for the luminescence yield and for the absolute absorption cross-section (i.e., the extinction coefficient) of the luminescing species, it is possible to calculate the chemical potential difference required to generate the luminescence. This should be of use in examining mechanisms in electroluminescence, chemiluminescence, and bioluminescence.

ACKNOWLEDGMENTS

I thank Martin Gouterman for pointing out the existence of the Russian work, M. P. Klein for a critical reading of the manuscript, and Professor Melvin Calvin for his guidance and interest.

*This work was supported, in part, by the U. S. Atomic Energy Commission.

[1]P. T. Landsberg, Thermodynamics (Interscience Publishers, New York, 1961).

[2]R. T. Ross, J. Chem. Phys. 45, 1 (1966).

[3]W. Shockley and H. J. Queisser, J. Appl. Phys. 32, 510 (1961).

[4]W. Shockley, Electrons and Holes in Semiconductors (D. Van Nostrand Company, Princeton, 1950).

[5]J. Tauc, Photo and Thermoelectric Effects in Semiconductors, transl. by M. Lauer (Pergamon Press, Oxford, 1962).

[6]M. Planck, Theory of Heat Radiation, transl. by M. Masius (Dover Publications, New York, 1959).

[7]E. H. Kennard, Phys. Rev. 11, 29 (1918).

[8]E. H. Kennard, Phys. Rev. 28, 672 (1926).

[9]Yu. T. Mazurenko and B. S. Neporent, Opt. i Spektroskopiya 12, 571 (1962). [English transl: Opt. Spectry. 12, 317 (1962)].

[10]B. I. Stepanov, Doklady Akad. Nauk S.S.S.R. 112, 839 (1957). [English transl.: Soviet Phys.--Doklady 2, 81 (1957)].

[11]B. S. Neporent, Doklady Akad. Nauk S.S.S.R. 119, 682 (1958). [English transl.: Soviet Phys.--Doklady 3, 337 (1958)].

[12]I. Ketskemety, J. Dombi, and R. Horvai, Ann. der Phys. 463 (Folge 7, Band 8), 342 (1961).

[13]W. van Roosbroeck and W. Shockley, Phys. Rev. 94, 1558 (1954).

[14]D. E. McCumber, Phys. Rev. 136, A954 (1964).

[15]See, for example, S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities (Addison-Wesley Publishing Company, Reading, Mass., 1959).

[16]E. Merrit, Phys. Rev. 28, 684 (1926).

[17]L. A. Kratsov and A. N. Rubinov, Opt. i Spektroskopiya 12, 636 (1962). [English transl.: Opt. Spectry. 12, 355 (1962)].

[18]T. S. Moss, Optical Properties of Semiconductors (Academic Press, New York, 1959).

[19]E. R. Washwell and K. F. Cuff, Radiative Recombination in Semiconductors, Seventh Int. Conf. on the Physics of Semiconductors, Paris (Academic Press, New York, 1964), p. 11.

[20]V. V. Gruzinskii and N. A. Borisevich, Opt. i Spektroskopiya 15, 457 (1963). [English transl.: Opt. Spectry. 15, 246 (1963)].

[21]R. T. Ross, Thesis, University of California, Berkeley (1966).

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