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Active Nitrogen

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Criticisms have been made of the ionic theory of active nitrogen, proposed by the author some years ago, on the ground that experiments carried out since then with the specific purpose of detecting N_2^+ ions in the glowing gas have yielded negative results. Need is felt therefore for re-examining the older theories in particular the atomic theory and its variations. It is shown in the paper that by collating the suggestions made in respect of this theory in recent years one may make the following hypothesis: Active nitrogen is a mixture of nitrogen atoms in the ground state ^4S and the metastable states ^2D and ^2P (the last named in small proportion) produced by dissociative recombination of N_2^+ ions and electrons always present in a strong electric discharge in nitrogen. The N_2^+ ions and electrons are thus the parent bodies of the active substance instead of being themselves the active substance, as had been proposed in the ionic theory. The reason the production of the atoms is supposed to be due to dissociative recombination and not to electronic bombardment of N_2 molecules, is that it has been known for a long time that the production of active nitrogen is closely associated with the presence and production of N_2^+ ions. The two outstanding properties of active nitrogen (besides its chemical activity) e.g., long-duration afterglow emitting its characteristic band spectrum, and the invariable presence of ionization in the glowing gas, are thus explained as follows: The nitrogen atoms recombine by a preassociation process (as first suggested by Gaydon) to produce N_2 molecules in the high vibrational levels of the B state from which the first positive bands, with the characteristic intensity distribution, are emitted. The long life of the afterglow is explained as resulting from the fact that the wall recombination of the N atoms is prevented by the formation of an adsorbed layer of N_2 molecules on the wall surface. (Formation of such an adsorbed layer was also assumed in the ionic theory.) The invariable presence of ionization in the glowing gas is explained as resulting from ionizing recombination of metastable atoms, $N(^2D)+N(^2P)\rightarrow N_2^+ + e$. Possible explanations of the negative temperature coefficient of the glow intensity, of the so-called dark modification, and also of some of the other properties of active nitrogen, are suggested.

1. INTRODUCTION. THE IONIC THEORY

The author of this note put forward some time ago the theory that the active substance in the well-known nitrogen afterglow (Lewis-Rayleigh type) consists of a mixture of N_2^+ ions and electrons.[1,2] The theory further postulated that the walls of the afterglow vessel are so conditioned by the formation of an adsorbed "layer" (probably of N_2) that only a small fraction of the impinging electrons attach themselves to the walls to form electronic surface charge. The neutralization of ions and electrons on the surface (which is a very fast process) being thus prevented, the recombination takes place mainly in the volume by a three-body process,

$$N_2^+ + e + M \rightarrow N_2(\text{excited}) + M(\text{excited}),$$

in course of which the characteristic afterglow spectrum is emitted. Here M is the third body (a nitrogen molecule) which takes up the excess of energy and momentum. The three-body collision process being necessarily a slow one, the long life of the afterglow is explained.

Critisicms of this "ionic theory" of active nitrogen have been made from time to time mainly on grounds of newer experimental results. These are as follows:

In 1948 Worley[3] carried out experiments to detect absorption, in the visible range, in a long column of the glowing gas (13 meters). It was expected that the transition $N_2^+(X')+h\nu\rightarrow N_2^+(A')$ would cause strong absorption because the reverse transition, $N_2^+(A')\rightarrow N_2^+(X')+h\nu$, is an allowed one leading to the emission of the familiar first negative bands in strong nitrogen discharge. The obvious inference from the experimental result is that N_2^+ ions are not present in sufficient number in the glowing gas.

Very recently Benson[4] has carried out interesting measurements of some of the physical properties of active nitrogen employing modern microwave techniques. He concludes from his results that the observed ionization in a stream of active nitrogen is incidental rather than essential to the production of the Lewis-Rayleigh afterglow (an opinion expressed also by other workers) and that the ionization appears to be due mainly to electrons. Further, the concentration of the electrons in the glowing gas is many orders less than that of the active particles.

In view of these criticisms is becomes necessary to re-examine some of the older theories of active nitrogen.

2. THE OLDER THEORIES

The oldest theory of active nitrogen is that the active substance in the afterglow is nitrogen atoms. The suggestion was first made by Rayleigh[5] in 1911 and is a very natural one since hydrogen afterglow—albeit of much shorter duration—is known to be due to recombination of hydrogen atoms. Sponer[6] in 1925 gave the theory a more definite form by suggesting that the

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[1] S. K. Mitra, Science and Culture (Calcutta) **9**, 46 (1943–44); Nature **154**, 212 (1944).

[2] S. K. Mitra, *Active Nitrogen—A New Theory* (Indian Association for the Cultivation of Science, Jadavpur, Calcutta, 1945). Part I gives a summary of the properties and phenomena of active nitrogen.

[3] R. Edwin Worley, Phys. Rev. **73**, 531 (1948).

[4] James M. Benson, J. Appl. Phys. **23**, 757 (1952).

[5] Lord Rayleigh (Strutt), Proc. Roy. Soc. (London), **A85**, 219 (1911).

[6] H. Sponer, Z. Physik **34**, 622 (1925); **41**, 611 (1927).

nitrogen atoms recombine by a three-body process,

$$\mathrm{N+N+M \rightarrow N_2(excited)+M(excited)},$$

in course of which the afterglow is emitted. If the excited nitrogen molecule be assumed to be formed in the higher vibrational levels of the $B\,^3\Pi_g$ state, then the emission of the afterglow spectrum (first positive bands) is explained (see Fig. 1). The reaction is energetically possible if Gaydon's value[7] of dissociation energy of the N_2 molecule (9.76 ev) is accepted. Further, since three-body collision is a slow process, the long life of the afterglow is explained. The reaction, however, does not explain why only selected bands of first positive group (see below) are emitted.

To obviate this difficulty Cario and Kaplan[8] proposed that the active substance in the afterglow is a mixture of metastable molecules in the *A* state, and metastable atoms in ^2P and ^1D states. [The energies of these states are 3.56 ev and 2.37 ev, respectively, (see Fig. 2).] It is supposed that the molecule in the *A* state is excited to the *B* state (from which the characteristic first positive bands are emitted) by collision with a metastable atom. Since the energy of the *A* state is 6.1 ev, the enhancement of selected bands of the first positive group is explained (see below).

There have also been rather speculative theories[9–11] suggesting that the active substance is a molecule in some highly metastable state or is a "collision complex (NN)" formed of two metastable nitrogen atoms.

The main concern of the above theories had been to explain the excitation of the characteristic afterglow spectrum and, to some extent, its long life. They do not make any attempt to explain the many other properties and phenomena of active nitrogen. This was first done in the ionic theory proposed by the author. But unfortunately, as already mentioned in the introduction, experimental evidence seems to go against the existence of N_2^+ ions and electrons, in sufficient numbers at least, in the glowing gas. It will however be shown in the next section that it is possible to develop a theory (an atomic theory) in which the N_2^+ ions and electrons, though they are not themselves the active substance, are the parent bodies of the same, namely metastable nitrogen atoms. This metastable atomic theory, unlike the theory of Cario and Kaplan, does not require the essential presence of the metastable molecules to explain the afterglow spectrum. It will further be shown that it is possible to explain by this theory not only the two outstanding properties of active nitrogen (besides its chemical activity), namely the long-duration afterglow emitting its characteristic spectrum and the invariable presence of ionization in the glowing gas, but also the other characteristics like negative temperature coefficient and the so-called dark modification.

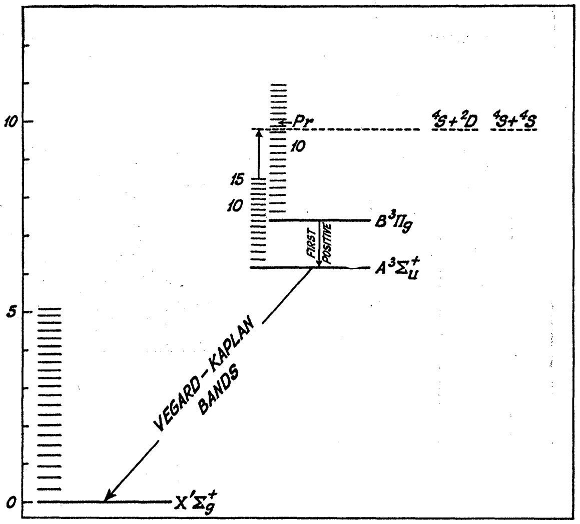

FIG. 1. Energy levels of N_2 molecule which are of interest in the emission of the Lewis-Rayleigh afterglow. The molecule in the excited *A* state dissociates when the energy of the vibration level is 9.76 ev. The two dissociated nitrogen atoms are in the ground state (^4S) if the dissociation energy is 9.76 ev, or one atom in the ground state and the other in the metastable ^2D state if the dissociation energy is 7.38 ev. There is predissociation of the excited molecule in the *B* state at the vibration levels $v=13$ to 16.

3. METASTABLE ATOM THEORY

It will be helpful and instructive if the statement of the theory is preceded by a little inductive reasoning.

One of the most firmly established facts in the whole group of phenomena of active nitrogen is that the spectrum of the Lewis-Rayleigh afterglow consists only of selected bands of the first positive group ($B^3\Pi_g \rightarrow A\,^3\Sigma_u$) as originate from the higher vibrational levels $v''=12$, 11, 10, etc. The energy of the highest vibrational level is about 9.7 ev. The intensity distribution in the bands differs, in fact, markedly from that in the spectrum of the ordinary glow discharge when active nitrogen is *not* being produced.

From the above fact one may at once infer that the active substance, whatever may be its nature, must be producing N_2 molecules in the higher vibrational levels of the *B* state even after the discharge is cut off.

Let us therefore consider the probable mode of production of such excited N_2 molecules in the glowing gas.

Detailed study of the N_2 band spectra shows that there is predissociation of the $N_2(B)$ molecule at the vibrational levels $v=13$ to 16 (Fig. 1). The predissociated products may be two nitrogen atoms in the ground state $N(^4S)$ if Gaydon's value of dissociation energy (9.76 ev) is accepted, or one atom in the ground state $N(^4S)$ and the other in the metastable $N(^2D)$ state if the older value of dissociation energy (7.38 ev) is assumed. Now corresponding to predissociation there is also the opposite process of preassociation in which the dissociated atoms, when they collide, have a probability of combining to produce the molecule in the

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[7] A. G. Gaydon, Nature **153**, 407 (1944).

[8] G. Cario and J. Kaplan, Z. Physik **58**, 769 (1929).

[9] R. T. Birge, Phys. Rev. **23**, 294 (1924).

[10] D. E. Debeau, Phys. Rev. **61**, 668 (1942).

[11] A. van der Ziel, Physica **1**, 353 (1934); **4**, 373 (1937).

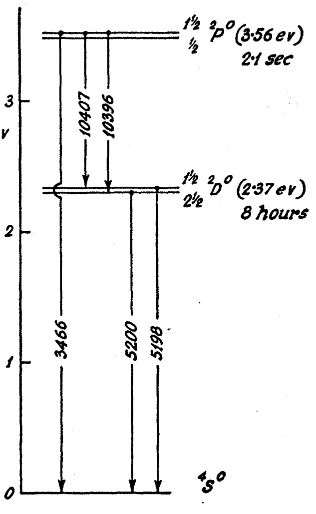

FIG. 2. Energy levels of the metastable states of the nitrogen atom. Nitrogen atoms in the ground and metastable states (which constitute active nitrogen) are produced by dissociative recombination of N_2^+ ions and electrons.

vibrating electronic state in which the predissociation occurred. The dissociated N atoms will, therefore, have a probability of recombining by radiationless transition in one of the high vibrational levels near $v=13$. The possibility of the production of excited N_2 molecules from which the characteristic emission of the afterglow spectrum takes place by such preassociation of N atoms has been discussed by Gaydon.[12] (The $N_2(B)$ molecules may also be produced by radiative recombination of two metastable N atoms. But the probability of such recombination is extremely small.)

Next let us consider how the N atoms—assuming that they constitute the active substance in the afterglow—may be produced in the discharge tube. No definite suggestion regarding this is made in the older theories. Perhaps there was the tacit assumption that the N_2 molecules are dissociated by impacts of high energy electrons. This however does not explain the fact—as observed by many workers—that the production of N_2^+ ions is closely associated with the production and the presence of the active substance. We may cite here two instances of such observation.

It has been observed by Rayleigh[13] that the yield of active nitrogen is the highest in the neighborhood of the cathode of the discharge tube. Also it is well known that the concentration of the positive ions is also the highest in the neighborhood of the cathode.

Kenty and Turner[14] found that in order to produce active nitrogen, one has to bombard nitrogen gas by electrons of energy 16.3 ev which is just above the first ionization potential of N_2. They further found that the maximum effect begins when the energy is nearing 20 ev, which is a little above the second ionization potential of N_2, 18.75 ev. This indicates that the bombarding electrons are producing N_2^+ ions in the excited A' state from which the first negative bands are emitted.

The essential presence of N_2^+ ions in the production of the active substance, the N atoms, can be understood if we assume that they are produced by dissociative recombination of N_2^+ ion and electron as follows:

$$N_2^+ + e \rightarrow N(\text{excited}) + N(\text{excited}).$$

Such dissociative recombination process has, according to Bates,[15] a very high probability. The dissociated N atoms may both be in the ^2D state or one in the ^2D and other in the ^2P state. The energy relations in the reaction are as follows: The energy released by recombination is the equivalent of 15.58 ev, the first ionization potential of N_2. The energy taken up on the right-hand side is the dissociation energy of N_2, 9.76 ev (Gaydon's value) plus the energies of excitation of the two atoms. The latter, if both the atoms are in ^2D state, is 4.74 ev, or if one of the atoms be in the ^2D and the other in the ^2P state, is 5.93 ev. In the first case there is an excess of 1.08 ev of energy, and in the latter there is a defect of 0.11 ev. The defect in the latter case can be made up if, as suggested by the author of this note,[16] the recombining N_2^+ ion be in a low vibrationality excited state or simply, as suggested by Bates,[17] if the colliding electron is sufficiently energetic. Of the two metastable states, ^2D has a very long life (about 8 hours), and hence it does not easily drop to the ground state. The ^2P state on the other hand has a life of about 2.1 seconds only and can drop to the ground state by radiation or by collision with the wall. It may be noted in this connection the line λ3466 due to the transitions $^2P \rightarrow {}^4S$ has been observed by Kaplan[18] in the spectrum of the strong discharge which produces active nitrogen. (With the older value of the dissociation energy, both the dissociated N atoms may be in the ^2P state.)

It is to be mentioned, that Kaplan, in discussing the behavior of the spectrum of the special types of intense short-lived nitrogen afterglows (which may properly be called Kaplan afterglow) discovered by him, has suggested that excited N atoms, as may be produced by dissocivative recombination of N_2^+ ions, play a part not only in these special types of afterglow, but also probably in the Lewis-Rayleigh afterglow.[18]

In view of the above discussion we may state our metastable atom theory as follows.

The active substance in the glowing nitrogen gas (Lewis-Rayleigh afterglow) is a mixture of nitrogen atoms in the ground state ^4S and in the metastable states ^2D and ^2P (the last named in only small proportion) produced by dissociative recombination of N_2^+ ion and electron produced under strong electric discharge.

It is to be noted that this mode of production of N

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[12] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1947), p. 160.

[13] Lord Rayleigh (Strutt), Proc. Roy. Soc. (London), **A92**, 438 (1916).

[14] C. Kenty and L. A. Turner, Phys. Rev. **32**, 799 (1928).

[15] D. R. Bates, Phys. Rev. **78**, 492 (1950).

[16] S. K. Mitra, Nature **167**, 897 (1951).

[17] D. R. Bates (private communication).

[18] J. Kaplan, Phys. Rev. **73**, 484 (1948).

atoms provides a link between the metastable atom theory as now formulated and the ionic theory as had been previously suggested the author of this note. The N_2^+ ion and electron are, as it were, the parent bodies of the active substance though they are not themselves so directly.

Let us now discuss how far this metastable atom theory explains the various properties and phenomena of active nitrogen.

4. DISCUSSION[19]

Wall Effect and Long Life

The life of the afterglow is known to depend markedly on the condition of the wall surface of the containing vessel. All workers agree that the formation of a "layer" on the wall promotes the production and prevents the destruction of the active substance. In the proposed theory the parent bodies of the active substance being N_2^+ ions and electrons, their recombination on the wall may be prevented if on the wall surface there is an adsorbed layer of molecules with little electron affinity. Only a small fraction of the electrons striking the wall will then be able to attach themselves to the wall to form an electronic surface charge. An adsorbed layer of N_2 molecules may have such a property. Further, such a layer would also prevent the destruction of the active substance, that is, prevent the recombination of the N atoms on the surface. One may imagine that the production itself of the adsorbed layer of N_2 molecules is a result of wall recombination of the N atoms.

The inhibition of the recombination of the N atoms on the wall at once explains the long life of the glow because recombination by the preassociation process, $N(^4S)+N(^4S)\rightarrow N_2\ ^3\Pi_g$, cannot be a fast one.

Chemical Activity

The chemical activity of active nitrogen consists generally in the formation of nitrides of the substance introduced (in the form of vapor) into the glowing gas. Since nitrogen in the atomic state is highly active, the chemical activity is at once explained.

Spectroscopic Excitation

This consists of excitations of the spectra of the substances introduced and also of the compounds formed of the same. The latter is easily explained as the molecule of nitride may be formed in an optically excited state. For the former however one has to assume a three-body collision process as follows:

$$N+N+M\rightarrow N_2+M(\text{excited}),$$

where M is the atom of the substance introduced. The maximum energy imparted by the active substance in spectroscopic excitation is known to be 9.52 ev. With Gaydon's value of the dissociation energy, this amount will be available on the recombination of the two atoms in the ground state. With the older value, however, one of the atoms at least has to be in the metastable ^2D (or ^2P) state.

Ionization

Ionization is always associated with the glow: The decrease of the one is accompanied by the decrease of the other, though the rates are not the same. Further, the ionization persists—being diminished only by a few percent—even after the glowing gas from the discharge has been drawn through the space between a pair of electrodes ("ion trap") across which a saturation current is flowing. This observation shows that either the ion trap is ineffective in stopping the flow of ions from the discharge or that the ions are being generated in the glowing gas. The author of this note held the former view in connection with his ionic theory. One may however explain the production of ions and electrons according to the metastable atom theory as follows.

It has been postulated that the metastable atoms are produced by dissociative recombination of N_2^+ ions and electrons. Corresponding to this process we can also imagine the reverse one, namely ionizing recombination of two metastable atoms

$$N(^2D)+N(^2P)\rightarrow N_2^++e.$$

As already indicated, there is enough energy available for this reaction to occur with Gaydon's value of the dissociation energy. With the older values of the same, there is a deficit of 1.08 ev even if both the atoms are in the ^2P state. But this may be supplied by the relative kinetic energy of the colliding atoms.

Negative Temperature Coefficient

If the temperature of the glowing gas is lowered keeping the pressure constant, then making allowance for the increase in intensity due to increase in concentration of the active substance, the reaction rate is found to increase. Heating decreases the intensity of the glow.

These effects may be explained if it is recalled that the predissociation of the two nitrogen atoms occurs in the vibration levels between $v=13$ and 16 of the B state. At higher vibrational levels the predissociation disappears. This means that for the converse process of preassociation, the colliding atoms must not possess relative kinetic energy much larger than that with which they were separated at predissociation. It is possible that the lowering of the temperature brings the kinetic energy of more atoms within this limit and thus increases the chance of preassociation. This increased chance more than compensates for the decrease of the rate of preassociation through the decrease in

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[19] Accounts of the various afterglow and active nitrogen phenomena, as discussed in this section, are to be found in reference 2.

the number of collisions caused by the lowering of the temperature. The opposite phenomenon occurs on heating and thus explains the decrease of the glow intensity with increase of temperature.

Dark Modification

It has been found that though heating destroys the glow it does not destroy the chemical activity of the glowless gas, or its ability to excite the spectrum of substances introduced in it. The considerations in the preceding sub-section regarding the effect of heating provide a simple explanation of this so-called dark modification of active nitrogen. The heating affects only the rate of preassociation of the atoms (which produces the afterglow); it cannot affect in any way their chemical activity or their ability to excite the spectra by three-body collision.

Besides the above, there are many other characteristic phenomena of active nitrogen, detailed explanations of which are not attempted here.

For example, in regard to the formation of the adsorbed layer on the surface, it is well established that contamination of the nitrogen used with some foreign gas in very small proportion, promotes the afterglow. It is possible that the contaminating gas acts as a catalytic agent to the formation of the layer. (The contamination which is most commonly used for promoting the afterglow in oxygen.)

Again according to Rayleigh's measurements, when the decay of the glow occurs mainly in the volume (the destruction of the active substance on the wall being kept at a minimum by special treatment of the wall and by use of large vessels), the law of decay is that for bimolecular reaction. This is as it should be according to the present theory. However, other experiments of Rayleigh show that, if the glowing gas is compressed or rarefied, the glow intensity varies as the cube of the concentration. This is a characteristic of termolecular reaction and cannot be reconciled with the theory. The same remark applies to the observation that increasing the concentration of the inert gas, keeping that of the active substance constant, increases considerably the intensity of the glow. Perhaps spectroscopic considerations of the preassociation process will provide explanations of these phenomena.

The question of the energy content of the active substance, in reference to Rayleigh's experiments of the heating of metal foils in the glowing gas, has also to be considered. According to Rayleigh, the energy imparted is at least 12.9 ev per act of destruction of the active substance on the metal foil. To explain this one has to assume that nearly all the molecules in the glowing gas have been dissociated and that metastable atoms are taking part in the surface recombination. (In later experiments Rayleigh obtained values even higher than 12.9 ev.) It is not possible to reconcile these observations with the metastable atom theory. Perhaps, as many of the investigators in this field maintain, the heating effect observed by Rayleigh was due to cathode rays in addition to the action of the active substance.

There is one point regarding the afterglow spectrum which appears to be puzzling. The spectrum does not show the Vegard-Kaplan bands, though the emission of the first positive bands leaves the molecules in the A state. It is of course agreed that since the $A \rightarrow X$ transition, yielding the Vegard-Kaplan bands, is a forbidden one, these bands will not ordinarily be observed. However, it is to be remembered that they have been identified by Kaplan in the special short-lived nitrogen afterglow studied by him. One would therefore have expected that the Vegard-Kaplan bands, though not ordinarily observable in the Lewis-Rayleigh type of afterglow, could be obtained by suitable adjustments of pressure and wall condition. However, though the Lewis-Rayleigh glow has been studied over wide ranges of pressures and wall condition, no trace of the Vegard-Kaplan bands has been found. (It may be argued that neither have emissions due to transitions of the N atoms from the metastable states been observed. But it is to be remembered that the ^2D state has the extraordinarily long life of 8 hours and that the ^2P atoms are present only in small number.) One explanation of the absence of the Vegard-Kaplan bands may be (as suggested by Cario and Kaplan[8]) that the N_2 molecules in the A state, before they have a chance of dropping to the X state by radiation, are raised to the B state by collision with the ^2D atoms,

$$N_2(A)+N(^2D)\rightarrow N_2(B)+N(^4S).$$

The energy relation shows that the $N_2(B)$ molecule will be formed in the high vibrational levels as required. The Cario-Kaplan process may therefore also contribute to the maintenance of the afterglow.

5. CONCLUDING REMARKS

The metastable atom theory of active nitrogen as developed in the preceding sections appears to give satisfactory explanations not only of the long life and the emission characteristic of the afterglow spectrum, but also of the other important associated properties, such as the invariable presence of ionization in the glow, the negative temperature coefficient, and the dark modification. The metastable atom theory may thus be an acceptable theory of active nitrogen. The author, however, feels diffident in making a more categorical statement regarding the merit of the theory, as his experience with the fate of the ionic theory (which he had developed in elaborate detail) warns him of the many pitfalls awaiting the unwary investigator of this elusive substance. What is now needed is a more thorough spectroscopic examination of the predissociation of $N_2(B)$ molecule, because there still appears to be some difference of opinion about its exact nature.

A straightforward proof of the theory would be to prove experimentally the presence of nitrogen atoms in the glowing gas (after the discharge has been cut off). Since the nitrogen atom possesses resonance lines near 1200A, absorption experiments in this region with a long column of the glowing gas would furnish this proof. Experiments to study this absorption are in progress under the direction of Professor G. Herzberg.[20] If the experiments prove the presence of nitrogen atoms in sufficient concentration in the glowing gas, the long series of speculations regarding the nature of active nitrogen will be ended.

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[20] G. Herzberg (private communication).

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The Solubility of Silicon and Germanium in Gallium and Indium*

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The solubilities of silicon and germanium in liquid gallium and in indium were determined over a wide temperature range. If the logarithms of the solubilities are plotted against the inversed absolute temperatures, straight lines are obtained the slopes of which yield the heats of solution. For the investigated systems it was found that the heats of solution are approximately proportional to the third power of the radii of the solvent atoms. Upon slow cooling of the saturated solutions silicon and germanium crystals of fair purity were obtained. The solubility data are of interest for the preparation of junction transistors.

KLEMM and co-workers[1] studied the phase diagrams of the systems Si-Ga and Si-In among others. The diagrams are of eutectic type and indicate for high temperatures an appreciable solubility of silicon in liquid gallium and indium which drops sharply with decreasing temperature. Apparently no published data are available in the temperature range where only small solubilities occur. Since we were interested in the crystallization of silicon from solutions in gallium and in indium, the solubility over a wide range of temperatures covering essentially the range of small solubilities was determined.

Gallium or indium was heated to a predetermined temperature in a quartz tube, using argon as an inert atmosphere. A piece of pure silicon was attached to a quartz hook and was kept immersed in the melt until saturation had been reached. The undissolved silicon was then pulled out of the melt and the apparatus cooled to room temperature. The amount of silicon which had dissolved at the test temperature was obtained from the difference in weight. Since the determination by weight was not accurate enough for values smaller than 0.1 atomic percent the lowest solubilities were measured spectrochemically.[2]

The solubilities of silicon in gallium and indium are plotted in Fig. 1 together with the data given in Klemm's paper. The logarithms of the solubilities in the concentration range below 10 atomic percent silicon when plotted against the inversed absolute temperature are fairly well represented by straight lines, the slopes of which yield the heats of solution at saturation, given in Table I.

For high concentration a marked deviation from a straight line takes place which is larger for silicon dissolved in indium than for silicon in gallium. Near 100 atomic percent silicon the slope of the solubility curve seems to approach the heat of fusion of silicon which is represented in Fig. 1 by the slope of line "Si."

Corresponding solubility measurements were made with the systems Ge-Ga and Ge-In. The experimental method used was the same as described above. However, a Pyrex tube was substituted for quartz glass since the temperature range under study was from 200 to 500°C only. Figure 2 is a plot of the results. It includes also the data of Klemm and co-workers.[1] As with silicon the solutions behave ideally in the range of low concentrations and the slopes of the straight lines yield the heats of solution at saturation. For high concentration

TABLE I. The heats of solution at saturation and the radii of the solvent atoms for the systems Si-Ga, Si-In, Ge-Ga, and Ge-In.

Heat of solution in kcal/mole	Atomic radii[a]	$\Delta H/r^3$
$\Delta H_{\mathrm{Si\ in\ Ga}} = 16.2$	$r_{\mathrm{Ga}} = 1.35$	6.6
$\Delta H_{\mathrm{Si\ in\ In}} = 25.8$	$r_{\mathrm{In}} = 1.57$	6.7
$\Delta H_{\mathrm{Si\ fusion}} = 9.46^{a} - 11.1^{b}$	$r_{\mathrm{Si}} = 1.17$	5.9–6.9
$\Delta H_{\mathrm{Ge\ in\ Ga}} = 8.3$	$r_{\mathrm{Ga}} = 1.35$	3.4
$\Delta H_{\mathrm{Ge\ in\ In}} = 11.9$	$r_{\mathrm{In}} = 1.57$	3.1
$\Delta H_{\mathrm{Ge\ fusion}} = 8.3^{b}$	$r_{\mathrm{Ge}} = 1.39$	3.1

[a] H. D. Hubbard and W. F. Meggers, *Periodic Chart of the Atoms* (W. W. Welch Scientific Company, Chicago, 1950).

[b] L. L. Quill, *The Chemistry and Metallurgy of Miscellaneous Materials* (McGraw-Hill Book Company, Inc., New York, 1950), Table 3.7, p. 28.

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* Presented at the American Physical Society Meeting at Cambridge, Massachusetts, January 22, 1953.

[1] Klemm, Klemm, Hohmann, Volk, Orlamuender, and Klein, Z. anorg. Chem. **256**, 239 (1948).

[2] The authors are indebted to Mr. J. Mellichamp for carrying out the spectrochemical analysis.