

After using for some weeks a thermometer constructed as described, the points at 0° and at -78.5° were found to be unchanged, indicating that there had been no leakage of air past the mercury.

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Possible Limits for the Heat of Dissociation of Oxygen.—The ionization of oxygen to form singly charged oxygen molecules has been found to occur at about 16 v. by Lockrow and Duffendack¹ and by Smyth.² In their study of the low-voltage arc in oxygen, Lockrow and Duffendack find a marked strengthening of lines and the appearance of new lines at 19.5 v.,³ and they ascribe this to dissociation and simultaneous ionization of one atom.¹ Smyth, working at low pressures and using his method of positive-ray analysis, did not find oxygen atom ions below 23.0 v.

For the similar process in hydrogen Smyth showed that the appearance of atom ions depended on a secondary process involving collisions, since by changing the pressure in the impact region, the voltage at which atom ions appeared could be greatly altered, this voltage decreasing as the pressure increased, until atom ions appeared at the same point as molecule ions.

Returning to the case of oxygen, in view of the fact that at very low pressure, oxygen atom ions do not appear until a considerably higher voltage is reached than that at which they appear at the relatively large pressures used in the low-voltage arc, it would seem probable that excited oxygen molecule ion can dissociate into oxygen atom and oxygen atom ion upon collision with some neutral particle, provided that its energy is greater than, or equal to, the energy change represented in such a process of dissociation. Now, atom ions are not found to occur at 16 v. and, therefore, unless the state of the molecule ion corresponding to 16 v. is metastable, for some special reason not being able to dissociate upon collision, the 16 v. molecule ion does not possess the energy necessary for the dissociation. The molecule must possess more energy than that represented by 16 v. to be able to dissociate upon collision. It appears that at 19.5 v. the excited molecule ion has sufficient energy to undergo this change upon collision. It may well be, however, that the energy increase represented in the dissociation is less than that corresponding to 19.5 v., but that under 19.5 v.

¹ Lockrow and Duffendack, *Phys. Rev.*, **25**, 110 (1925).

² Smyth, *Proc. Roy. Soc. (London)* **105A**, 116 (1924).

³ Communicated by Dr. Duffendack in a letter to the author.

there is no state of the molecule ion the energy of which is greater than that corresponding to the dissociation. Again, there may be such a state, but it may be metastable, one which upon collision will not undergo dissociation. Considering, then, that this value may be somewhat greater than that strictly required in the change alone, a maximum value can be calculated for the heat of dissociation of oxygen; and a minimum value can be determined, since no atom ions occur at 16 v.

These calculations can be made in the familiar way from the following simple thermochemical considerations. The reactions in question can be represented by the following equations.



Subtracting (2) from (1) there results



The heat of ionization corresponding to Equation 2 can be found from the ionization potential of the atom, which has been determined spectroscopically by Hopfield⁴ to be 13.56 v. This corresponds to a heat of ionization of 312,600 cal. per mole. The heat of dissociation and simultaneous ionization of one atom corresponding to Equation 1 is not greater than the energy corresponding to 19.5 v. which is 450,000 cal. per mole, and not less than that corresponding to 16.0 v. which is 369,000 cal. per mole, for the reasons given above. The difference in the first case is 137,400 cal. and in the second 56,400 cal. Therefore, the heat of dissociation of molecular oxygen into atomic oxygen is not less than 56,400 cal. per mole and not greater than 137,400 cal. per mole. While these limits are wide, it is believed that they are narrower than could be given heretofore.

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Germanium. XI. Germanium Glasses. Preliminary Note.—The positions of silicon and germanium in Mendeléeff's Periodic Table make it evident that close analogies between the compounds of the two elements are to be expected. The compounds of germanium which have thus far been isolated and studied, in particular the hydrides, the halides, germanium tetra-ethyl and germanium chloroform, bear out this view,

⁴ Hopfield, *Nature*, **112**, 437 (1923).