posited as a thin film upon the surface of the article and the walls of the container. This film may serve as a support and conduction pathway for a subsequent layer of electrolytically deposited copper.

The method finds some objection in the expense of the reducing agent employed.

The reaction is simply the formation of cupric hydroxide and its immediate reduction by the excess of hydrazine.

$$CuSO_4\ N_2H_42H_2O\ Cu(OH)_2\ N_2H_6SO_4$$
$$2Cu(OH)_2\ N_2H_4{\cdot}2H_2O\ 2Cu\ N_2\ 6H_2O$$

The rapidity of the reaction allows for the formation of a hydrosol which gradually precipitates due to the presence of the bivalent $SO_4$ ion. When a suspension of cupric hydroxide is used instead of the sulphate the precipitation is much slower.

However, the same effect is obtained by addition of an alkali to the hydrazide of copper. This substance, prepared by treatment of potassium hydrazine carbonate with dilute copper sulphate, is a blue, amorphous, insoluble powder, of empirical formula $CuN_2H_6$. It shows all the qualitative reactions of a hydrazide.

ROBERT D. BARNARD

UNIVERSITY OF CHICAGO

## SPECIAL ARTICLES

### ON THE APPARENT LARGE DIAMETERS OF MOLECULES FOR DEACTIVATION BY COLLISION

A RECENT paper by Tolman, Yost and Dickinson[1], devoted mainly to a criticism of some of the underlying physical assumptions made by Fowler and Rideal[2] in a theoretical study dealing with the rate of maximum activation by collision for complex molecules, with particular reference to its application to velocities of gas reactions, takes up the question of the apparent large diameters for deactivation-collisions to which the latter theory seems to lead.

The purpose of this note, in addition to one or two other observations, is to point out an error in Tolman, Yost and Dickinson's calculation on $N_2O_5$. In agreement with Fowler and Rideal they show that the fraction of molecules possessing energy greater than ε₀ in a system containing N molecules per c. c. each molecule having s variables (coordinates or momenta) which contribute classical square terms to the internal energy, is

$$N_{act.} = N \frac{1}{\Gamma(\frac{1}{2}s)} \left(\frac{\varepsilon_0}{kT}\right)^{\frac{1}{2}s-1} e^{-\frac{\varepsilon_0}{kT}}$$

If the maximum possible rate of deactivation by collision with unactivated molecules is given by

$$Z_{deact.} = 4\,N\,N_{act.}\,\sigma^{*2} \sqrt{\frac{\pi kT}{m}}$$

and if the principle of microscopic equilibrium holds, the maximum possible rate of activation by collision with unactivated molecules according to these authors, is given by

$$Z_{act.} = 4\,N^2\sigma^{*2} \sqrt{\frac{\pi kT}{m}}\, \frac{1}{\Gamma(\frac{1}{2}s)} \left(\frac{\varepsilon_0}{kT}\right)^{\frac{1}{2}s-1} e^{-\frac{\varepsilon_0}{kT}}$$

$\sigma^*$ being the mean diameter for a deactivation by collision. $\varepsilon_0$ is connected with the heat of activation q in the Arrhenius expression by the relation

$$\varepsilon_0 = q + (\tfrac{1}{2}s - 1)kT$$

$s = 14$; $T = 300°K$; $Q = 24{,}700$ calories; $\frac{Q}{RT} = \frac{q}{kT} = 41.5$; and $\frac{\varepsilon_0}{kT} = 47.5$. By substitution one obtains for the rate of activation:

$$Z_{act.} = 4\,N^2\sigma^{*2} \sqrt{\frac{\pi \times 8.3 \times 10^7 \times 300}{108}} \left(\frac{1}{6!}\right)\left(47.5\right)^6 e^{-6}.\,e^{-\frac{Q}{RT}}$$
$$= 4.25 \times 10^9\,\sigma^{*2}\,N^2\,e^{-\frac{Q}{RT}}$$

The rate of decomposition as found by Hirst and Rideal[3] is

$$2.53 \times 10^{14}\,N\,e^{-\frac{Q}{RT}}$$

taking $N = 1.615 \times 10^{15}$ molecules per c. c. at 0.05 mm. Hg. and 300°K. and assuming equality in the two rates,

$$\sigma^* = 6.07 \times 10^{-6}\ \text{cm.}$$

or about 15 times that to be expected from kinetic theory values. Tolman, Yost and Dickinson's value for the same calculation is $4.7 \times 10^{-4}$ cms. or nearly 1,000 times greater than kinetic theory values. The difficulties they point out with respect to large diameters are thus greatly reduced in significance especially when we remember that several other cases of large effective radii are known. MacNair[4] calculates the effective diameter of excited Cd atoms as $3 \times 10^{-6}$ cms. from observations on depolarization effects. By comparing the per cent. of polarization of $D_2$ resonance radiation in sodium vapor at $10^{-6}$ mm. pressure excited by polarized light, with that predicted by the Heisenberg theory, Datta[5] finds that the effective diameter of the colliding atoms is of the order of magnitude $10^{-4}$ cm. or over 1,000 times the kinetic theory value. Similarly Schütz[6] calculates the effective diameter of a collision between normal mercury atoms and mercury atoms in

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[1] Proc. Nat. Acad. of Sci. *13*, 188, 1927.

[2] Proc. Roy. Soc. *113*, 571, 1927.

[3] Proc. Roy. Soc. *109*, 526, 1925.

[4] Phys. Rev. *29*, 677, 1927.

[5] Zeit. f. Physik. *37*, 625, 1926.

[6] Zeit. f. Physik. *34*, 260, 1925.

the $2^3P_1$ state to be 8 times kinetic theory value. Stuart[7] finds the effective radius of collisions between mercury atoms in the $2^3P_1$ state with foreign gases to be $5.9 \times 10^{-8}$ cm. MacNair[4] concludes that the largest effective radii are observed in depolarizing influences of neighboring atoms. In cases of transfer of energy between atoms not quite in resonance smaller effective radii are observed while with totally dissimilar atoms colliding the effective radii are still less. We would expect therefore that with $N_2O_5$ molecules in random distribution the effective radii would be somewhat larger than given by kinetic theory.

I would like to point out, that while collisions between inactive molecules are not considered to occur any more frequently than is usual in kinetic theory, yet collisions between active and inactive molecules which cause a transfer of energy and which may result in deactivation, are observed to occur 50 to 66 times as often as is given by kinetic theory using data for the radii of normal and excited atoms. (Schütz[6]). This indicates that the apparent abnormality in diameter for deactivation by collision can be accounted for by increased numbers of collisions. This point might bear consideration. Now it must be observed that the deactivational diameter calculated in the above fashion, presumes 100 per cent. efficiency for deactivation collisions, an assumption to which I am unable to subscribe any more than to assume that every collision resulting in a certain degree of activity causes the molecule to decompose. In a recent paper[8] I have shown that only one in 100,000 molecules of azo-methane which may be sufficiently activated, actually decomposes. We are thus in a position to understand more readily that the large deactivational diameters are only apparent and not real. Consider the reverse of the reaction:

$$A + B \rightleftarrows A_{act.} + B_{inact.}$$

If every collision resulted in the deactivation of $A_{act.}$, then the effective target area or diameter would turn out to be quite large, but if we give a kinetic theory value to the diameter of $A_{act.}$ we may then calculate the efficiency of deactivation. Another way of looking at the same thing is to say that on ordinary kinetic theory, an efficient process would appear to have larger effective target areas than an inefficient process.

Bernard Lewis
*National Research Fellow*
School of Chemistry,
University of Minnesota.
May 15, 1927

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[7] Zeit. f. Physik. *32*, 262, 1925

[8] Proc. Nat. Acad. Sci. *13*, 546, 1927.

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## POLLEN STERILITY IN PEACHES

The writer has previously reported[1] the pollen sterility of the J. H. Hale variety of peach, and in the *Proceedings* of the International Conference on Plant Sterilities is reported some results on the inheritance of sterilities. In the latter paper, it is stated that of 127 seedlings secured from open-pollinated blossoms of J. H. Hale, 42, or 33 per cent., were pollen sterile, judging by the appearance of the anthers and by germination tests.

In the spring of 1926, a number of seedlings resulting from controlled crosses, using J. H. Hale as the seed parent, have bloomed, and because of the interest in this subject, the counts are given herewith.

| Parentage | Population | Bloomed | Sterile | Per cent. |
|---|---|---|---|---|
| J. H. Hale × 43215 (Elberta × Greensboro) | 111 | 63 | 31 | 49.2 |
| J. H. Hale × Marigold (Lola × Arp) | 184 | 106 | 35 | 33.0 |
| J. H. Hale × 27116 (Slappey × Dewey) | 132 | 120 | 0 | 0.0 |
| J. H. Hale × 32816 (Carman × Slappey) | 193 | 178 | 0 | 0.0 |

Chinese Cling, which is pollen sterile, is probably the seed-parent of Elberta, and Elberta is probably the seed-parent of J. H. Hale. Greensboro and Carman are probably direct descendants from Chinese Cling and Lola and Slappey are probably indirect descendants. Dewey is believed to be of another group or race, and this latter group or race is probably involved in the parentage of Slappey and possibly of Elberta.

It is interesting that in the above crosses where a seedling of Slappey parentage was used no pollen sterile seedlings have, so far, occurred. In the progeny of J. H. Hale × 43215 and J. H. Hale × Marigold, there is an apparent difference in the ability of the pollen parent to produce maleness in the progeny, but there remain enough seedlings which have not bloomed to overcome this difference, and the latter eventuality is altogether within the bounds of reason.

C. H. Connors
New Jersey Agricultural
Experiment Station,
New Brunswick, New Jersey

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[1] Connors, C. H., "Fruit-setting on the J. H. Hale Peach in New Jersey Agricultural Experiment Stations," 43d Ann. Rpt., p. 102, 1922.