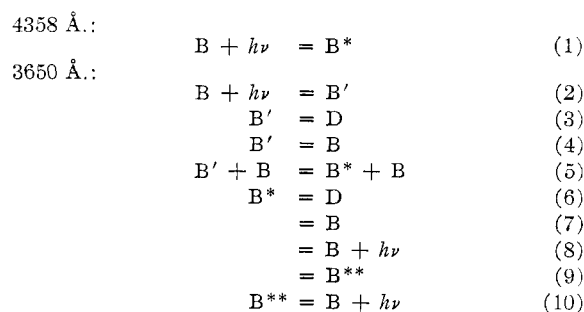## Discussion

It is seen that $R_{CH_4}/R_{C_2H_6}^{1/2}$ (B) (where R represents rate in molecules per milliliter per second and (B) is the concentration of biacetyl in molecules per milliliter) is reasonably constant at a given temperature, although possibly there is a slight trend at 198°. This would indicate that methane and ethane are formed by customary reactions.[8]

The following points should be noted: (1) primary yields at 4358 Å. are essentially independent of intensity from 125 to 198°. This is in contrast to the results at room temperature[2]; (2) primary yields at 3650 Å. decrease with increase in pressure at 124°. At 198° the trend is uncertain but small. This correlates with the fluorescence efficiency which increases with increase in pressure.[9]

The detailed mechanism of Bell and Blacet[3] will not be repeated, but for sake of discussion the mechanism used to interpret the fluorescence will be given[10]

4358 Å.:

$$B + h\nu = B^* \qquad (1)$$

3650 Å.:

$$\begin{aligned}
B + h\nu &= B' & (2) \\
B' &= D & (3) \\
B' &= B & (4) \\
B' + B &= B^* + B & (5) \\
B^* &= D & (6) \\
&= B & (7) \\
&= B + h\nu & (8) \\
&= B^{**} & (9) \\
B^{**} &= B + h\nu & (10)
\end{aligned}$$

At 4358 Å. the following relationships are found.

(a) $\phi/Q = k_6/k_9$ if reaction (9) is assumed not to be reversible. (Q = fluorescence efficiency.) This relationship is valid at 100° since neither ϕ nor Q change appreciably with pressure.[2,10]

(b) A plot of log (ϕ/Q) vs. $1/T$ shows an activation energy difference of 16.5 kcal. The ratio of frequency factors is 4×10.[9]

(c) $(1 - \phi - Q)/Q = (k_7 + k_8)/k_9$. A plot of the logarithm of this function vs. $1/T$ gives an activation energy difference of 7.1 kcal. (It should be noted that only the green, long lived fluorescence efficiency has heretofore been studied.)[10] Thus if k_8 is small compared to k_7, as it should be since the blue fluorescence efficiency is very low, the activation energy difference between k_7 and k_9 is approximately 7.1 kcal. a_7/a_9, the ratio of pre-exponential factors, is about 3×10^5 by extrapolation.

(d) By subtraction one finds $E_6 - E_7 = 9.4$ kcal. The ratio of pre-exponential factors a_6/a_7 is about 10^4.

By combining the above relationships one finds

$$1/Q - 1 = 4 \times 10^9 \exp(-16500/RT) + 3 \times 10^5$$
$$\exp(-7100/RT) \quad (11)$$

since $(1 - \phi - Q)/Q = (1/Q - 1) - \phi/Q$. Equation 11 reproduces satisfactorily the fluorescence data from 75 to 200°.

(8) See R. E. Varnerin, THIS JOURNAL, **77**, 1426 (1955).

(9) H. J. Groh, Jr., *J. Chem. Phys.*, **21**, 674 (1953). This article gives references to an earlier work.

(10) N. A. Coward and W. A. Noyes, Jr., *ibid.*, **22**, 1207 (1954).

Thus at 4358 Å. the fluorescence data and the photochemical primary yields as calculated by equation 14 of the previous article can be related to each other. This does not prove, of course, that the detailed mechanism is correct, but it does show that the mechanism fits the facts now known at this wave length.

At 3650 Å. the following relationships are found.

(a) Equation 24 of the previous article states that a plot of $1/\phi$ vs. (B) at constant temperature should give a straight line. This assumes that dissociation from (3) predominates over that from (6). This relationship is valid at 124° but at 200° the apparent primary yield does not change with pressure. This may indicate that (6) has become important but since there are doubts about the calculation of the primary quantum yield further speculation is not warranted.

(b) In the previous article Q/ϕ is proportional to (B) at 30°. This assumes dissociation to be due to (3). At 200° the fluorescence efficiency increases with pressure, but the apparent primary yield does not change. Hence this relationship is not valid if the method of calculating the primary yield is correct.

Little more can be said about interpretation either of the fluorescence yields or of the primary photochemical yields at the present time. A method of obtaining the primary yields with precision is badly needed. It is not obvious how these can be obtained since addition of foreign molecules such as iodine, oxygen and nitric oxide will almost certainly change these yields. If all products, including those of minor importance, were known and a completely valid mechanism established, possibly primary yields could be calculated. Such a method would necessitate an accuracy hitherto not attained in quantum yield measurements and a full understanding of diffusion and of wall effects.

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Reaction at High Temperatures between Air and Liquid Metal Solutions Containing Sodium. Effect of Solution Composition

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Studies have been made of the reaction between air at room temperature and jets of liquid metal solutions containing sodium at temperatures of 600 to 800°. The reactivity of these solutions showed a marked dependence on solution composition. This behavior is reported here.

The method of study was as follows. A heated alloy was ejected downward through a small orifice into a large steel chamber. The chamber had previously been evacuated and filled with dry air at a pressure of one-fourth to one atmosphere to give a measured dew point of −43°. In all experiments the amount of oxygen in the chamber was from three to thirty times the amount required for complete oxidation of the sodium present. The time-of-flight of a jet through the reaction chamber

was always sufficiently short so that only a fraction of the sodium that could react did so. These jets contained a significant quantity of small droplets as shown in motion pictures taken at 700 frames per second.

Experimental Results.—The following binary solution systems were studied: sodium–bismuth, sodium–cadmium, sodium–indium, sodium–lead, sodium–mercury, sodium–silver and sodium–tin. The reaction between air and a jet of a sodium solution was usually vigorous. It was accompanied by a flame, a dense smoke of reaction products and, when especially high temperatures and large sodium contents were used, a weak explosion.

Solutions of sodium and bismuth reacted vigorously with air when the sodium concentrations were high. However, at lower sodium concentrations and sufficiently low temperatures, the reaction was negligible as evidenced by the absence of both flame and smoke and recovery of the substantially unreacted alloy.
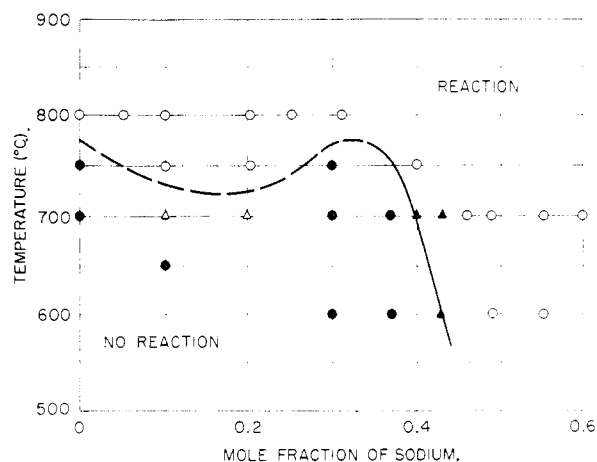

Fig. 1.—Temperature *vs.* composition diagram for sodium–bismuth solutions; the points represent experimental results as follows: ○, reaction; ●, no reaction; △, very slight reaction; ▲, some tests slight reaction, some tests no reaction. The curve separates the region of reaction from the region of no reaction.

A temperature *vs.* composition diagram for liquid sodium–bismuth solutions is presented in Fig. 1. The curve approximately separates the region of reaction from the region of negligible reaction. Circles and triangles on this diagram represent the temperature–composition values at which tests were conducted. Most represent two to four tests each. Unshaded circles represent tests in which reaction occurred, while those which are shaded showed no reaction. Each shaded triangle represents a group of tests of which part showed some reactivity, while the rest showed no reactivity. The unshaded triangles represent tests which always showed a very slight reaction. The dotted portion of the curve is poorly defined inasmuch as it may actually pass beneath the unshaded triangles rather than above them as shown. Jets of pure bismuth showed appreciable reactivity at 800° but not at 750°. The curve is to some extent, no doubt, a function of the experimental conditions and a different technique would probably give somewhat different ignition temperatures.

The reactivity of sodium–mercury solutions was likewise dependent on composition. At both 600 and 700° the line of no reactivity lay between sodium mole fractions of 0.25 and 0.35. The test method was less sensitive for solutions containing mercury than for solutions containing bismuth especially at temperatures above 700° because of the formation of a dense fog of mercury.

When the air was saturated with water vapor, the line of zero reactivity was shifted toward lower sodium concentrations by a small but appreciable amount for both sodium–bismuth and sodium–mercury solutions. Changing the pressure of the air from one atmosphere down to one-quarter atmosphere did not produce an appreciable change in the reactivity of either sodium–bismuth or of mercury solutions.

The five other binary systems listed above were tested only at 700° in dry air at one atmosphere pressure for a mole fraction of sodium of 0.1. All these systems were quite reactive.

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