manner that 80–90% of the calciferol was in the precipitate and the rest in the washings. The pyridine calciferyl sulfate precipitate was found to be slightly soluble in petroleum ether by employing the above criteria in subsequent experiments. These experiments were confirmed by employing 50 mg. of calciferol and weighing the amount of calciferol in the petroleum ether washings which were washed free of any traces of pyridine sulfur trioxide by water. The precipitate was treated with potassium hydroxide in water (using 4–6 moles of the base for each mole of sulfur trioxide employed in the original reaction) and extracted repeatedly with petroleum ether. The petroleum ether fraction was washed free of potassium hydroxide and taken to dryness. There was no potassium or sulfate in the residue, which was found to contain all the calciferol as shown by the mercuric acetate test and later by gravimetric procedure. These relations were also established by the animal experiments using the technique previously outlined [Natelson and Sobel, above].

Thus, it appears that the potassium hydroxide hydrolyzes the pyridine calciferyl salt whereas in the ergosteryl and cholesteryl salts the pyridine is displaced by potassium in a double decomposition and the extremely insoluble potassium sulfate derivative is formed. The reaction for calciferol may be illustrated

$$\mathrm{StOH} + \mathrm{SO_3C_5H_5N} \xrightarrow{\mathrm{C_5H_5N}} \mathrm{StOSO_3OHC_5H_5N}$$

$$\mathrm{StOSO_3OHC_5H_5N} + 2\mathrm{KOH} \longrightarrow \mathrm{StOH} + \mathrm{C_5H_5N} + \mathrm{K_2SO_4}$$

The reaction was next applied to cod liver oil concentrate. Two grams of the concentrate (containing 73.333 I. U. per g. obtained through the courtesy of the National Oil Products Co.) was dissolved in 4 cc. of pyridine and followed by the addition of 1 g. of pyridine sulfur trioxide, heated at 46° for one hour and 50 cc. of petroleum ether added, and then allowed to stand for three days in an ice-box. A yellowish white precipitate settled which was washed with cold petroleum ether. The precipitate was then treated with potassium hydroxide in the presence of petroleum ether. Two fractions of sterols were obtained, one the insoluble potassium steryl sulfates and the other the petroleum ether soluble fraction. The latter was evaporated down to dryness in the presence of maize oil and used for bio-assay. A vitamin bio-assay was run comparing the activity of this fraction against the original material, the unreacted fraction of the concentrate and the insoluble potassium steryl sulfate. It was found by this criterion that approximately 60% of the original vitamin D content precipitated and was found later in the petroleum ether fraction while the insoluble potassium sulfate does not contain any vitamin D. Thus a simple method for obtaining a high concentration of natural vitamin D was obtained. Further work is in progress at present to isolate a pure vitamin D from natural sources.

PEDIATRIC RESEARCH LABORATORY
THE JEWISH HOSPITAL OF BROOKLYN
BROOKLYN, N. Y.
RECEIVED MAY 18, 1936

COMMUNICATIONS TO THE EDITOR

SURFACE IONIZATION OF CESIUM ON TUNGSTEN

Sir:

Alterum, Krebs and Rompe [*Z. Physik*, **92**, 1 (1934)], in an article on the surface ionization of cesium on a tungsten filament, have reported obtaining values of 0.21 at 1520°K. and 0.29 at 1830°K. for its degree of ionization. These values are considerably lower than the ones predicted by theory for these temperatures; they also show an increase in the degree of ionization occurring with rising temperature, whereas theory predicts a decrease. The apparatus used by Alterum, Krebs and Rompe was one in which the ionization unit was surrounded by the saturated vapor of cesium. Taylor and Langmuir [*Phys. Rev.*, **44**, 423 (1933)], using the same type of apparatus, previously had obtained values approximating 100% ionization at temperatures as high as 1500°K. Above this temperature the onset of a very large photoelectric current from plate to filament, caused by the action of the light from the filament on an adsorbed layer of cesium on the plate prevented them from extending their measurements further.

In view of these contradictory reports, it was decided to investigate the surface ionization of cesium by a different method. Copley and Phipps [*Phys. Rev.*, **45**, 344 (1934); **48**, 960 (1935)] found that the use of an atomic ray instead of saturated vapor almost entirely eliminated the photoelectric current in the case of potassium, and they were able to determine its degree of ionization up to a temperature of 2800°K. An apparatus similar to the one described by Copley and Phipps was constructed, its furnace was filled with carefully purified cesium, and the measurements were taken in the same manner as was described in the case of potassium.

According to statistical mechanics, the degree of ionization of cesium on tungsten is given by the expression

$$\frac{1}{1 + 2\exp\left[(I - \phi)\epsilon/kT\right]} \qquad (1)$$

where ϕ is the work function of tungsten at the temperature T, and I is the ionization potential of cesium. Curve A in Fig. 1 was obtained by plotting Eq. 1 with ϕ replaced by $\phi_0 + \alpha T$ where ϕ_0 is the work function at absolute zero and α is its temperature coefficient. The numerical values used for these constants (4.514 v. e. for ϕ_0 and 5.6×10^{-5} v. deg.$^{-1}$ for α) are the same as those which were found necessary to account for the results obtained with potassium. It is evident that the experimental values for the degree of ionization of cesium below 2000°K. are in satisfactory agreement with curve A. Furthermore, our results confirm those found in the low temperature range by Taylor and Langmuir. Curve B, which is shown for comparison, was obtained by plotting Eq. 1 assuming a negligible temperature coefficient of the work function.

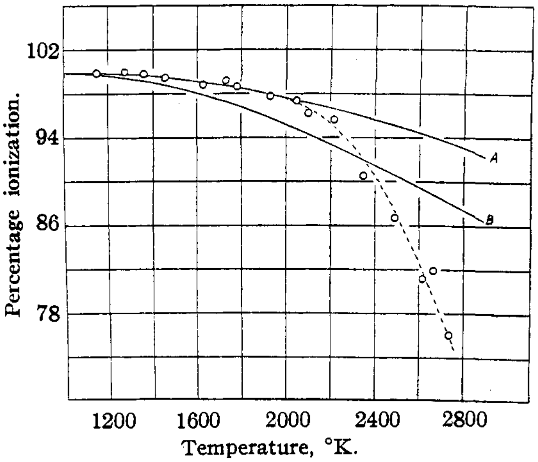

Fig. 1.—The percentage ionization of cesium on tungsten *versus* temperature.

Above 2000°K. the experimental values for the degree of ionization fell off too rapidly to agree with curve A. This behavior may be accounted for in part by experimental error caused by a photoelectric current, which, in spite of the use of the atomic ray, was present in this range of temperature. A similar rapid falling off of the ionization of potassium at temperatures above 2000°K. has been observed. This phenomenon is being further investigated by using atomic rays of potassium and sodium. Since these metals have higher ionization potentials than cesium, their surface ionization in the high temperature range may be more accurately measured.

DEPARTMENT OF CHEMISTRY M. J. COPLEY
UNIVERSITY OF ILLINOIS JULIAN GLASSER
URBANA, ILLINOIS

RECEIVED APRIL 17, 1936

KINETICS OF THERMAL CIS–TRANS ISOMERIZATIONS

Sir:

Kistiakowsky and Smith [THIS JOURNAL, **58**, 766 (1936)] have shown that the *cis–trans* isomerization of butene-2 appears to be of approximately first order during a run but of second order with respect to initial pressure. The purpose of this communication is to point out that when the equilibrium constant is approximately 1 as in this reaction, the rate in a given run for a bimolecular reaction would be indistinguishable from that calculated for a first order reaction.

If x is the concentration of the *trans* isomer, the net rate for a bimolecular reaction may be expressed by the equation $-\mathrm{d}x/\mathrm{d}t = Kx^2 - (1 - x)^2 = (K - 1)x^2 + 2x - 1$ where K equals K_1/K_2, the ratio of the rate constants for the forward and reverse reactions. If the equilibrium corresponds to $x = 0.5$, then $K = 1$ and $-\mathrm{d}x/\mathrm{d}t = +2(x - 0.5)$, which is the expression for a first order reaction. The deviations from this result are considerable for equilibrium mixtures differing only slightly from 50%, so it is desirable to make a calculation for the experimental value of $x = 0.528$ at equilibrium. This rate is given by $-\mathrm{d}x/\mathrm{d}t = -0.20x^2 + 2x - 1 = (x - 0.528)(-0.20x + 1.894)$. The first order rate would be proportional to $(x - 0.528)$ so the variations in