[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Temperature Scale of The Ohio State University Cryogenic Laboratory

BY THOR RUBIN, HERRICK L. JOHNSTON AND HOWARD ALTMAN

A constant-volume helium thermometer has been designed and developed as the primary temperature standard, for the temperature range 13 to 300°K., at The Ohio State University Cryogenic Laboratory. A series of calibration runs showed that the final temperature scale is accurate, in terms of the thermodynamic scale, to within 0.01° below 30°K., to within 0.02° up to 150°K., and to within 0.025° up to 300°K. This thermometer is used to calibrate, simultaneously, two copper–constantan thermocouples and a strain-free platinum–rhodium resistance thermometer, which serve as direct standards to calibrate instruments in use in the laboratory.

Introduction

To standardize and correlate experimental work conducted at The Ohio State University Cryogenic Laboratory, an accurate temperature scale was developed. The ice point of the scale was taken as 273.16°K., and other temperatures on the scale determined from ratios of the limiting PV products reduced to zero pressure by use of second and third virial coefficients for helium. The primary standard for the temperature interval 13 to 300°K. is a constant-volume helium thermometer. It is used to calibrate, simultaneously, two copper–constantan thermocouples, and a strain-free platinum–rhodium resistance thermometer,[1] which serve as direct standards to calibrate other instruments in the laboratory.

Description of the Helium Thermometer

The helium thermometer, similar in general design to the condensed gas calorimeter in use in this Laboratory,[2] is shown in Fig. 1. The copper thermometer bulb (A), whose calibrated volume is given in Table I, replaces the calorimeter of the calorimeter assembly. The lower (B), upper (C) and auxiliary (D) blocks are enclosed in a vacuum-tight brass container (E), which is suspended in a Pyrex dewar (F). The dewar, in turn, is set in a brass cryostat[3] (G) whose windows coincide with unsilvered strips in the dewar.

TABLE I

CALIBRATION OF THERMOMETER BULB AND 11.1-CM. LENGTH OF 0.0635-CM. I.D. STAINLESS STEEL CAPILLARY, AT 25°

Weight filled, g.	Weight empty, g.	Weight of water, g.	Vacuum correction	Volume of water, cc.
2104.527	1939.234	165.293		
2104.523	1939.237	165.286		
Average		165.289	0.171	165.946
Volume of thermometer bulb alone				165.904 cc.

The pressure within the thermometer bulb is measured by means of an external manometer (H), which communicates with the bulb through stainless steel capillaries. An 11.1-cm. section of 0.0635-cm. i.d. stainless steel capillary (I), silver-soldered into the boss at the upper end of the thermometer bulb, connects the bulb with a 364.51 cm. length of stainless steel hypodermic needle tubing (J), 0.0635 cm. o.d. by 0.0330 cm. i.d., which forms a part of the manometer system. The larger capillary is brought into thermal contact with the upper and auxiliary blocks by means of Cerrobend alloy, and the smaller capillary is inserted and soft-soldered into the larger one as it emerges from the auxiliary block. The total noxious volume of the capillaries amounts to 0.3187 cc. Five thermocouples, soldered to various points along the capillaries, permit the determination of the average temperature of the gas contained in this volume, and consequently a correction can be obtained for the amount of gas present in the capillaries during any standardization.

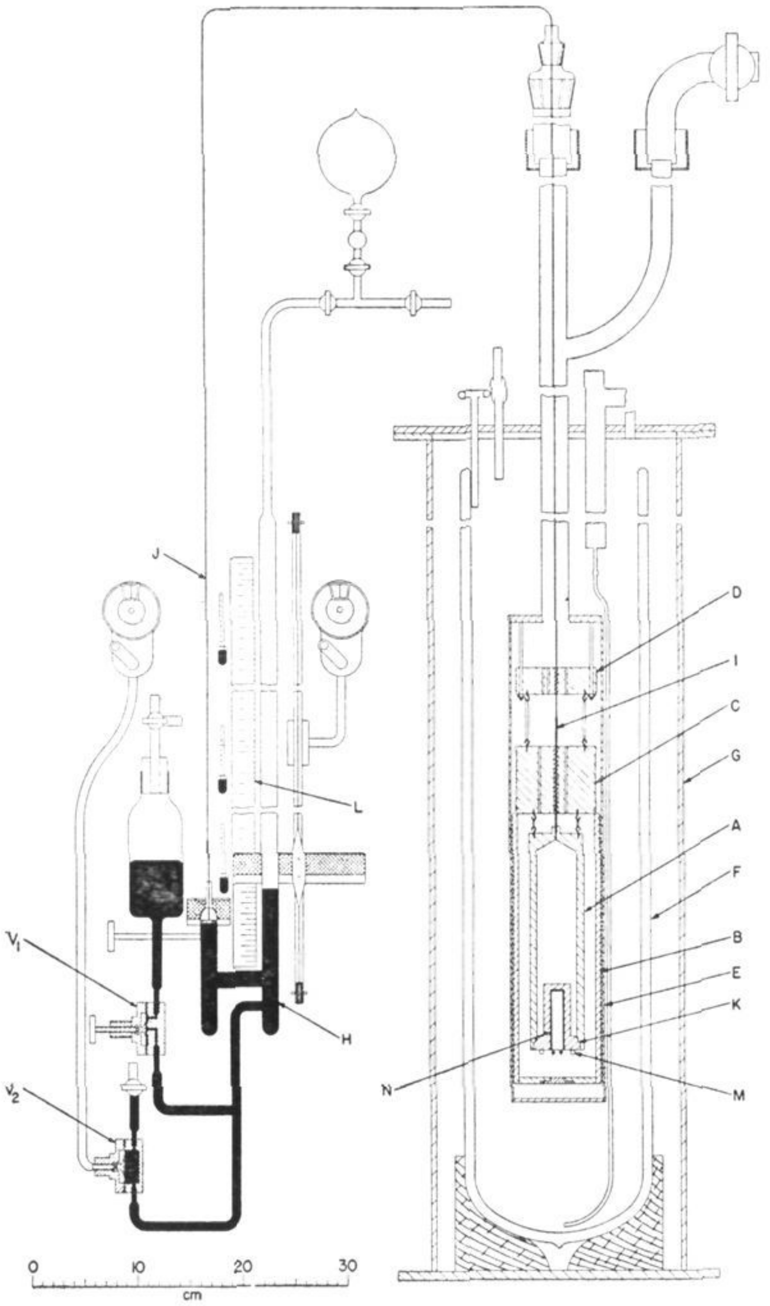

Fig. 1.—Constant-volume helium thermometer.

The wall and upper end of the thermometer bulb are turned from a solid bar of copper. The bottom is closed by tight-fitting copper plug (K), silver-soldered to the wall. Both the bottom plug and the stainless steel capillaries, mentioned above, are soldered in an atmosphere of helium so that the highly finished interior of the thermometer is not subjected to atmospheric oxidation during soldering. The plug contains a re-entrant well into which fits the platinum resistance thermometer.

The thermometer bulb is wound with double nylon covered No. 40 B. and S. gage gold (+0.15% silver) wire, cemented to the bulb by G. E. Adhesive No. 7031. The entire bulb is covered with gold leaf to minimize heat transfer by radiation. The space around the bulb and around the blocks, and the capillary, is evacuated to at least 10^{-5} mm. during all runs.

Manometer and Mercury Handling System.—Accurate pressure readings are made by means of a large-bore mer-

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(1) T. Rubin, H. Altman and H. L. Johnston, *Rev. Sci. Inst.*, to be published.

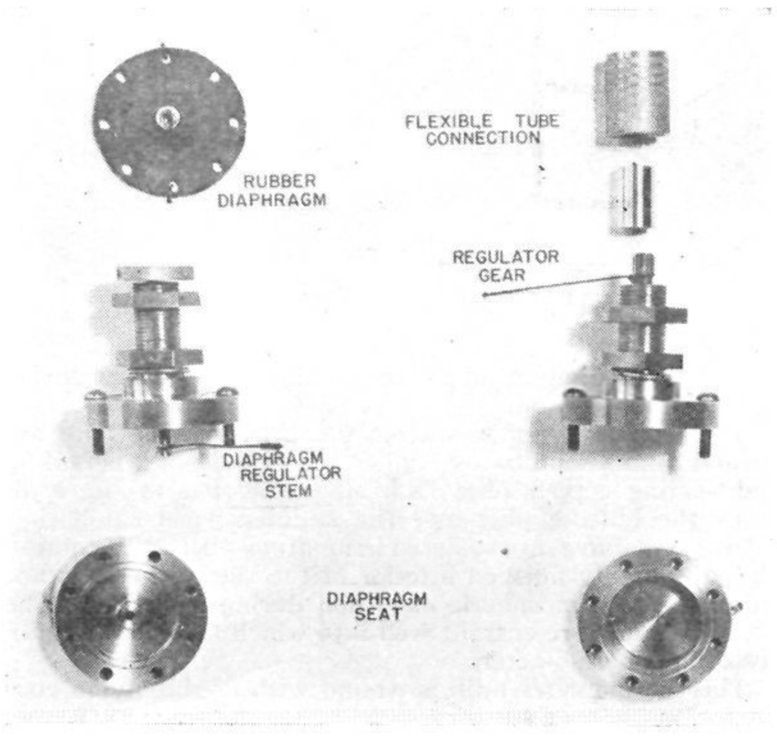
(2) H. L. Johnston, John T. Clarke, E. B. Rifkin and E. C. Kerr, THIS JOURNAL, **72**, 3933 (1950).

(3) H. L. Johnston, *Rev. Sci. Inst.*, to be published.

cury manometer with the aid of a standard steel meter bar (L) and a Gaertner M-904 cathetometer. The vertical arms of the H-shaped manometer are made from 15.59 mm. i.d. pyrex tubing of uniform bore. The short arm of the manometer is drawn out and sealed to a short length of glass capillary, through which passes the stainless steel capillary from the thermometer bulb. A stainless steel spindle, having a vertical needle point perpendicular to its lower surface, is waxed tightly to the inside of the manometer tube immediately below the capillary section and completely fills the upper end of the manometer arm down to a point where the bore is unaffected by glass blowing. A hole, 0.0330 mm. diameter, is drilled through the axis of the spindle and counterbored for a short distance near its upper end. The stainless steel capillary from the thermometer bulb is driven, *via* the bore of the glass capillary, into the counterbore so as to form a gas-tight seal between the spindle and the steel capillary.

The relatively small dead-space volume between the lower face of the spindle and the mercury surface, when the mercury just touches the needle point, was measured as a function of meniscus height by weighing the displaced mercury. It has been found to vary linearly from 0.982 cc. for a meniscus height of 1.10 mm. to 1.016 cc. for a meniscus height of 1.80 mm. Since the manometer is mounted in an enclosed case, whose temperature is recorded to within 0.1°, the amount of helium in the manometer dead space is accurately known for each run.

The mercury level within the manometer is controlled by a unique valve system. A special valve, shown in Fig. 2a (V_1 in Fig. 1), operates by remote control to regulate coarsely the amount of mercury in the manometer system at any one time. Since the meniscus in the short arm is always adjusted to the steel needle point so as to maintain a nearly constant dead space, mercury additions or withdrawals occur in the long arm, which is maintained under high vacuum. Fine adjustments, to within 0.01 mm. of the needle point, are made by means of the mercury displacer shown in Fig. 2b (V_2 in Fig. 2). This latter valve can change the mercury level in the short arm by as much as 5 mm. by changing the volume of the communicating mercury supply line. Parallel illumination of the mercury meniscus, obtained by front lighting, eliminates distortion of the meniscus. The manometer readings are corrected, by use of the "International Critical Tables," for the temperature of the mercury and of the standard meter scale and for capillary depression as measured by mensicus height. In addition, a gravitational correction, amounting to 980.101 for this locale, is applied.



Coarse adjuster A

Mercury displacer B

Fig. 2.—Valves for controlling mercury level in manometer.

Secondary Temperature Standards.—The three secondary standards in use in this Laboratory have been calibrated against the helium thermometer. These include two single-junction copper–constantan thermocouples patterned after those of Giauque, Buffington and Schulze[4] and a strain-free platinum–rhodium resistance thermometer described elsewhere.[1]

The two standard thermocouples, designated as TC 80 and TC 93, were selected from a lot of twelve which were made from single strands of double nylon covered No. 25 B. and S. gage Advance wire and of double silk covered No. 36 B. and S. gage copper wire. The Advance wire had passed the severe gradient test described by Giauque and coworkers,[4] with deflections of less than 2 microvolts, and the wire insulation was impregnated with G. E. Adhesive No. 7031, dried in air. These two standards are embedded in the Cerrobend low-melting alloy that fills the thermocouple tubes (M) soldered to the bottom of the helium thermometer bulb.

The copper case of the strain-free resistance thermometer (N of Fig. 1), designated as RT 4, forms a sliding joint with the re-entrant well in the bottom of the helium thermometer bulb and is held firmly in place by a set screw which projects diagonally into the well. Good thermal contact is insured by the use of stopcock grease. Over a period of two years, the ice point resistance of this secondary standard, 110.5403 ohms, remained constant to within 1 part in 275,000.

Electrical leads from the three standards, from the heaters, and from the control thermocouples emerge from the high-vacuum space surrounding the helium thermometer through slots around the periphery of the ground glass plug.

Operation of the Helium Thermometer.—Series calibrations were made with four separate fillings of helium, obtained from the Linde Air Products Co. who represented it to be spectroscopically pure. A mass spectrometer analysis, made in our laboratory, indicated that oxygen and nitrogen were present to less than 1 part in 100,000, with no detectable trace of water vapor.

The primary gas thermometer was filled with helium after evacuating it, through the manometer, to a static vacuum of less than 10^{-5} mm. Helium was allowed to enter the system through the manometer, while the mercury level was maintained below the level of the cross bar of the H. A fixed quantity of gas was trapped in the thermometer bulb, in the noxious volume, and in the manometer dead space, under pressures of 76 to 87 cm. with the entire system at room temperature, by introducing mercury into the manometer. After adjusting the temperature of the thermometer bulb to within 0.03° of the ice point, by bringing the reading of the standard resistance thermometer close to the ice point value, the pressure was accurately read on the manometer. The total amount of helium was then computed from the known volumes and the observed temperatures of the thermometer bulb, noxious volume, and manometer dead space.

By utilizing the virial coefficients recently determined in this Laboratory,[5] we calculated the amount of helium in the thermometer bulb from the equation of state

$$PV = n(RT + BP + CP^2) \qquad (1)$$

The amount of gas held in the noxious volume and in the manometer dead space, however, was computed by use of the Ideal Gas Law and found to be less than 1% of the total gas in the system. The ice point temperature and the gas constant, R, were taken as 273.16°K. and 82.0567 cc. atm./mole/deg., respectively. At the conclusion of each series of runs, usually a period of more than a week after the initial determinations, the amount of helium enclosed in the system was redetermined at the ice point, to check possible escape of the gas or changes in the constants of the apparatus. A summary of the ice point determinations for the four series of runs is given in Table II. The initial and final de-

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(4) W. F. Giauque, R. M. Buffington and W. Schulze, THIS JOURNAL, **49**, 2343 (1927).

(5) D. White, P. Camky, H. L. Johnston and T. Rubin, "Low Pressure Data of State for Helium," to be published.

terminations agree to within 1 part in 8,000 in all cases. It is evident that there was no leakage since the deviations with time are random with sign.

At temperatures other than the ice point, calibrations were made by regulating the temperature of the thermometer bulb and of the surrounding blocks to the approximate desired temperature and by reading simultaneously the resistance thermometer, the two thermocouples and the two manometer arms. Figure 3 illustrates the data for a typical run. Above 35°K., the drift rates for the thermometer bulb and blocks were no greater than 0.02°K. per hour, but below 35°, the drift rates were somewhat larger. In all instances, however, the drifts were uniform and no difficulty was experienced in selecting a common equilibrium time for each run to which all data could be related. The temperatures of the noxious volume, of the manometer dead space, and of the open mercury wells mounted adjacent to the manometer tubing were also taken, as a function of time.

Treatment of Data.—The total moles of helium used in any given series, final column of Table II, was reduced by the amount of helium held in the noxious volume and in the manometer dead space. This reduction was calculated in the same manner as described in the ice point determinations, and the result was reliable to within 1%. Since the total correction amounted to less than 1% of the enclosed helium at room temperature and diminished with increasing temperature, the error thus introduced into the final temperature scale amounted to no more than 1 part in 12,000 at room temperature and to less than 1 part in 40,000 at 60°K.

TABLE II

ICE POINT DETERMINATIONS OF THE MOLES OF HELIUM ENCLOSED IN THE THERMOMETER SYSTEM

Series	Run	Initial determination	Final determination	Average used
I	19–36	7.67061 7.67165 7.67063	7.67078	7.67070
II	37–76	7.75609	7.75518	7.75563
III	77–93	7.84896	7.85019	7.84957
IV	94–97	6.76167	6.76177	6.76172

A tentative value for the temperature of the thermometer bulb was computed by equation 1 from the bulb volume corrected for thermal contraction of copper,[6] from the residual amount of helium (n) contained in the bulb, from the observed pressure, and from a choice of virial coefficients[5] based on a preliminary estimate of the temperature. The final temperature value was ascertained after one or two successive approximations.

The foregoing has effectively defined our temperature scale by the relationship

$$T = 273.16(P^\circ V^\circ)/(P_0^\circ V_0^\circ) \qquad (2)$$

where $(P^\circ V^\circ)$ is the molal PV product, at temperature T, which is corrected for gas imperfection, and $(P_0^\circ V_0^\circ)$ is the corresponding corrected product at the ice point. This equation represents the true thermodynamic scale with a defined ice point, as recently proposed by Giauque.[7]

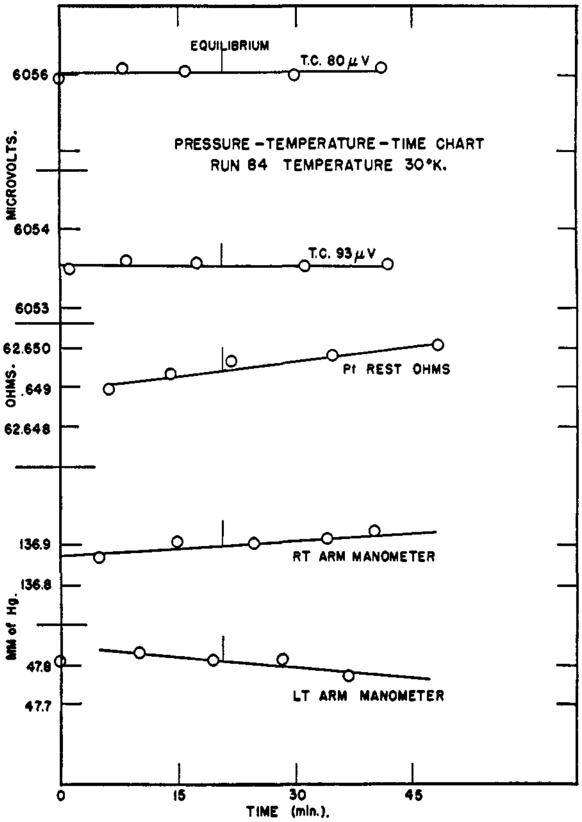

Fig. 3.—Graphical representation of calibration data for a typical run.

Consideration of all sources of error, principally small errors in pressure and in the amount of helium in the thermometer bulb, leads to the conclusion that temperatures determined by the helium thermometer are accurate to within 0.01° below 30°K., to within 0.02° up to 150°K., and to within 0.025° up to 300°K.

In terms of thermodynamic temperature, errors in the readings of the secondary standards are not much greater than those of the primary helium thermometer standard except at temperatures below about 25°K., since the resistance thermometer readings proved reproducible to 0.0005 ohm and those of the thermocouples to 0.04 microvolt. Below 25°K., the sensitivities of the secondary standards decrease rapidly. A large-scale plot of the resistance of thermometer RT 4 *vs.* its calibration temperature formed a smooth curve that fitted the points of all four series of measurements to within 0.02°. Similar plots for the thermocouples fitted smooth curves to within 0.05° at all temperatures and generally to within 0.02°.

A smooth curve of TC 80 data was used to construct an interpolation table which was then analytically smoothed at 1° intervals from 13 to 300°K. This table constitutes the working temperature scale for thermocouples in use in The Ohio State University Cryogenic Laboratory and is believed accurate in a thermodynamic sense to within 0.03° between 150 and 300°K. and to within 0.02° be-

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[6] W. H. Keesom, F. P. G. A. J. von Agt and A. F. J. Jansen, "The Thermal Expansion of Copper between +101° and −253°," Leiden Comm. 182a.

[7] W. F. Giauque, *Nature*, **143**, 623 (1939).

tween 30 and 150°K. Working thermocouples, used in various pieces of apparatus in the Laboratory, are from the same lot of wire as TC 80, and have been directly intercompared with TC 80 in the manner described by Giauque, Buffington and Schulze.[4] Calibration graphs of the small deviations from TC 80 are used to correct the readings of these couples to the Standard Table.

The smooth calibration curve of RT 4 is probably 0.005 to 0.01° more accurate than the Thermocouple Table. By comparing this thermometer with one recently calibrated at the National Bureau of Standards, we hope soon to have a comparison between our basic temperature scale and the one currently in use at the National Bureau of Standards.

An independent, although somewhat insensitive, check of our Standard Thermocouple Scale was recently provided by data of state carried out in this Laboratory for hydrogen and for nitrogen. Extrapolation of PV products to zero pressure and division by the figure 82.0567 cc.-atm./deg., the molal gas constant, yielded values for T that agreed in all cases with values computed from its thermocouple to within the accuracy of the PV extrapolations, namely, 0.05°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Effects of Substituents on the Rate of Hydrolysis of Triarylsilanes in Wet Piperidine

BY HENRY GILMAN AND G. E. DUNN

This investigation was initiated in order to compare the effects of a series of substituents on the rates of reactions occurring at analogous silicon and carbon atoms. Six new monosubstituted triphenylchlorosilanes were prepared and reduced to the corresponding triphenylsilanes. The rates of hydrolysis of these triphenylsilanes in wet piperidine were found to be in agreement with those predicted on the basis of Hammett's σ-constants, with the exception of that for diphenyl-*p*-dimethylaminophenylsilane. It was shown that the value of σ reported previously for the *p*-dimethylamino group is in error, and that two σ-constants are required for this group—one to be used with conjugated and one with non-conjugated side chains.

A little over twenty years ago Kipping, in reporting the failure of all his attempts to prepare organosilicon compounds containing silicon-to-silicon or silicon-to-carbon double bonds, noted that such compounds had never been isolated, and recorded his conclusion that "an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional circumstances."[1] Since that time, the complete absence from the literature of reference to any such compound has shown his belief to be well founded. Furthermore, several authors have pointed out the probability that resonance structures having such double bonds make relatively small contributions to the ground states of organosilanes.[2] Thus, while triarylmethyl cations, anions and free radicals are rendered relatively stable by the ability of such resonating systems to spread out electron surpluses or deficiencies, the corresponding triarylsilyl fragments are comparatively unknown.[3] These considerations indicated that electrical interactions between the silicon atom and other atoms or groups in a silane molecule might be different from those between the same atoms or groups and the corresponding carbon atom of an analogous carbon compound. It was the purpose of this investigation to study these differences by observing the changes in the rate of a reaction occurring on the silicon atom of an organosilane as a series of substituents were introduced into the molecule, and comparing these changes with the changes produced when the same series of substituents were introduced into a similar carbon compound.

Hammett has shown[4] that the effect of a meta or para substituent on the rate of a reaction occurring on the side chain of a benzene derivative can be represented by the equation

$$\log k - \log k^0 = \rho\sigma$$

where k^0 is the specific rate constant for the unsubstituted derivative and k is that for the substituted one. Rho is constant for any given type of reaction and σ is constant for any particular substituent. This generalization simplifies the comparison of organosilicon compounds with their carbon analogs. It is only necessary to measure the rates of reaction of a series of substituted aryl silanes and plot the logarithms of the specific rate constants against the σ-constants reported by Hammett. A linear relationship would indicate that the silicon and carbon atoms interact in the same way with other substituents in the type of molecule investigated. A non-linear relationship would indicate the reverse.

The reaction chosen for study was the basic hydrolysis of monosubstituted triarylsilanes. These compounds are easily prepared, are sufficiently

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(1) F. S. Kipping, *J. Chem. Soc.*, 104 (1927); F. S. Kipping, A. G. Murray, and J. G. Maltby, *ibid.*, 1180 (1929).

(2) (a) H. Gilman and G. E. Dunn, THIS JOURNAL, **72**, 2178 (1950); C. G. Swain, R. M. Esteve and R. H. Jones, *ibid.*, **71**, 965 (1949); (b) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(3) Siliconium ions have been proposed as intermediates in certain reactions of organosilanes by F. C. Whitmore, *Chem. Eng. News*, **26**, 672 (1948) and F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, THIS JOURNAL, **69**, 1551 (1947), but doubt has been cast upon the correctness of this interpretation by subsequent work. See Footnote 2a. Triphenyl- and triethyl-silyllithium were prepared by C. A. Kraus and H. Eatough, *ibid.*, **55**, 5008 (1933) and C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 195 (1934), respectively. However, it was found necessary to use a procedure much more involved than those commonly employed for the preparation of the corresponding carbanions, and the products were of a greater order of reactivity than their carbon analogs. Kraus and Eatough, *loc. cit.*, also reported the preparation of a solvated triphenylsilyl radical, but gave no evidence that their product actually contained an unpaired electron.

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chapter VII.