[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

Anion-exchange Studies. XXI. Th(IV) and U(IV) in Hydrochloric Acid. Separation of Thorium, Protactinium and Uranium[1,2]

By Kurt A. Kraus, George E. Moore and Frederick Nelson

Received December 16, 1955

The anion-exchange behavior of Th(IV) and U(IV) in hydrochloric acid solutions was investigated with a strong base quaternary amine resin. Adsorbabilities of these two elements are surprisingly different. Th(IV) shows no adsorption throughout the HCl concentration range studied (0.1 to 12 *M*). U(IV) shows negligible adsorption below 5.5 *M* HCl and rapidly increasing adsorbability at higher concentrations. The ion-exchange behavior of these elements is compared with that of other elements of oxidation number four. An anion-exchange method for the separation of Th(IV), Pa(V) and U(VI) has been devised, as well as a method for the separation of U(IV) and U(VI).

In continuation of the systematic survey of the anion-exchange behavior of the metals in hydrochloric acid solutions, the present paper summarizes the results with Th(IV) and U(IV). While U(IV) is adsorbed on a strong base anion-exchange resin from strong HCl solutions, Th(IV), surprisingly, shows negligible adsorption even in concentrated HCl solutions. This permits easy separation of Th(IV) from a large number of ions, including most ions of oxidation number +4. Further, ready separation of Th(IV) from Pa(V) and U(VI) can be achieved.

Experimental

As in earlier work, adsorbabilities were determined either by the column or equilibrium methods. The former was used when distribution coefficients *D* (amount per kg. resin/amount per liter solution) were low and the latter when they were high. The resin was from the same batch of quaternary amine polystyrene divinylbenzene resin (Dowex-1, *ca.* 200 mesh, *ca.* 10% DVB) which had been used in most of the earlier studies.

For the column method *ca.* 0.1-ml. aliquots of 0.1 *M* stock solutions of $ThCl_4$ or UCl_4 in HCl were added to small columns, usually 0.25 cm.^{2} × 4.0 cm. In some experiments with Th(IV), longer columns (15 to 20 cm.) were also used to increase the precision of the measurements. The columns were pretreated with appropriate HCl solutions. Appearance of Th(IV) in the effluent was determined by spot testing with "Thoron"[3] or radiometrically (Th^{234}, $\beta,\gamma,T_{1/2}$ = 24.1 d; Th^{230}, $\alpha,T_{1/2}$ = 80,000 y). Elution of U(IV) was determined visually (green) and concentrations determined spectrophotometrically or radiometrically (U^{233},$\alpha,T_{1/2}$ = 1.6×10^5 y). For the equilibration experiments with U(IV), *ca.* 10^{-3} *M* U(IV) solutions (prepared and stored under oxygen-free nitrogen) were introduced under nitrogen into 10 cm. spectrophotometer cells. A weighed amount of resin was added to the cells (under nitrogen) and the mixture shaken for several hours. The fraction of U(IV) adsorbed by the resin was determined spectrophotometrically (Beckman model DU quartz spectrophotometer), utilizing the prominent 648 mμ peak of U(IV)[4] after the resin had settled (or floated in concentrated HCl) in the cell. From these data the distribution coefficients *D* were calculated.

All experiments were carried out in an air-conditioned room at 25 ± 1°.

Results and Discussion

1. Adsorption of Th(IV) and U(IV).—Adsorption of Th(IV) was found to be negligible throughout the HCl concentration range studied (0.1–12 *M* HCl). In column experiments where small amounts of Th(IV) were used, Th(IV) appeared in maximum concentrations at *ca.* 0.4 column volumes of effluent, the approximate fractional interstitial volume of the columns. Similarly, up to *ca.* 5.5 *M* HCl, U(IV) appeared in maximum concentrations near 0.4 column volumes, indicating negligible adsorption. At higher HCl concentrations, the distribution coefficient of U(IV) rose rapidly to *ca.* 45 in 8 *M* HCl (low loading of resin) and *ca.* 500 in 11.3 *M* HCl (*ca.* 15% loading).

Adsorbability of Th(IV) was also measured in concentrated LiCl solutions, since considerably higher adsorbabilities are often found in these low acid media than in HCl solutions of similar concentration.[5] While negligible adsorption was found for 8.3 *M* LiCl–0.1 *M* HCl (elution maximum at 0.4 column volumes of effluent), slight but definite adsorption occurred in 12 *M* LiCl–0.1 *M* HCl (elution max. at 6 column volumes). These data suggest that Th(IV) forms negatively charged complexes to a slight extent in concentrated LiCl solutions, although the effect is too small to establish this unambiguously.

The large difference between the anion-exchange behavior of Th(IV) and U(IV) presumably implies a large difference in the stability of the negatively charged complexes, even though the stability constants of the first chloride complexes of these elements are approximately the same. Waggener and Stoughton[6] reported the concentration quotient $k_{01}^{m} = 1.53$ for Th(IV) (ionic strength $\mu = 1$) where $k_{01}^{m} = (MCl^{+3})/[(M^{+4})\ (Cl^{-})]$ and parentheses indicate concentrations. This value may be compared with $k_{01}^{m} = 2 \pm .5$ which was obtained by Ahrland and Larsson[7] for U(IV) at the same ionic strength. The properties of Th(IV) and U(IV) are often considered similar as, for example, implied

---

[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory. Part of this work has been reported earlier in Reports ORNL-336 (Chemistry Division Quarterly Report, Dec. 1948–Feb. 1949); ORNL-330, April 1949; ORNL-286 (Chemistry Division Quarterly Report, March–June 1949).

[2] Previous papers: (a) XIX. K. A. Kraus and H. O. Phillips, This Journal, **78**, 249 (1956); (b) XX. K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Volume 7, p. 113, Session 9B. 1, P/837, United Nations (1956).

[3] 1-(*o*-Arsonophenylazo)-2-naphthol-3,6-disulfonic acid (a) V. I. Kuznetsov, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 914 (1944); (b) P. F. Thomason, M. A. Perry and W. M. Byerly, *Anal. Chem.*, **21**, 1239 (1949).

[4] K. A. Kraus and F. Nelson, This Journal, **72**, 3901 (1950). In Fig. 1 the spectra were incorrectly labeled. Spectrum A is for Pu (IV) and spectrum B for U(IV).

[5] K. A. Kraus, F. Nelson, F. B. Clough and R. C. Carlston, *ibid.*, **77**, 1391 (1955).

[6] W. C. Waggener and R. W. Stoughton, *J. Phys. Chem.*, **56**, 1 (1952).

[7] S. Ahrland and R. Larsson, *Acta Chem. Scand.*, **8**, 137 (1954).

by their inclusion in a coherent series of elements, the actinides. Although the approximately equal stability of the positively charged complexes MCl^{+3} seems to bear out this similarity, the wide divergence of the stabilities of the negatively charged complexes tends to contradict it. The anion exchange work thus confirms the thesis that predictions regarding the properties of these elements, which are based on the assumption that they belong to a series of extremely similar elements, must be made with caution.[8]

The lack of correlation in the relative stabilities of the positive and negative complexes of these elements may be considered surprising. However, it is by no means unique. Thus a similar observation was made for the relative stabilities of the chloride complexes of the first row transition elements, particularly for Ni(II) and Co(II).[9] For these elements positively charged complexes (if they exist) must also have approximately equal stabilities, while the stabilities of the negatively charged complexes differ widely.

2. Comparison with Other M(IV) Elements.—Th(IV) appears to be the only metallic element of the fourth group which cannot be adsorbed by a strong base anion-exchange resin from concentrated HCl solutions and hence may readily be separated from these elements. For comparison, the adsorbabilities of a number of elements of oxidation number four are summarized in Fig. 1, a plot of log D *vs.* M HCl. Some preliminary experiments have also been carried out with Pb(IV). They indicated strong adsorption at high HCl concentrations. The data are not included in Fig. 1 since the instability of Pb(IV) precluded accurate measurements.

The data for Fig. 1 were collected using the same batch of resin. However, the results cannot be considered strictly comparable, at least at high values of D, since they were not all obtained at constant and low loading. However, they should be comparable for low values of D where in all cases loading was low. Thus, the data in Fig. 1 should give the relative adsorbabilities of these elements and probably also an index to the relative stabilities of their negatively charged complexes. The data for V(IV), Ti(IV) and Ge(IV) were taken from published work,[10] while those for Sn(IV), Zr(IV) and Hf(IV) have not previously been reported. Similar data for Zr(IV) and Hf(IV) have been published by Huffman and co-workers.[11] However, while they report a ratio of *ca.* 3.5 for $D_{\mathrm{Zr}}/D_{\mathrm{Hf}}$, present work indicates a ratio of *ca.* 10. Presumably, differences in the properties of the resins used (Dowex-2 *vs.* Dowex-1, cross-linking, etc.) are responsible for these relatively minor differences.

It can be seen from Fig. 1 that, of the M(IV) ions studied in some detail, Sn(IV) is most strongly adsorbed and shows excellent adsorption for M HCl $\geqslant$ 0.1. Ge(IV) shows significant adsorption ($D > 1$) above *ca.* 3.5 M HCl; U(IV) above 6 M HCl; Zr(IV) above 7 M HCl; Hf(IV) above 8 M HCl and Ti(IV) above 9.5 M HCl. V(IV) shows slight adsorption only in concentrated HCl,[10a] which might be sufficient for separation from Th(IV) with relatively long columns. In an experiment where all these elements would be added to a column in concentrated HCl and then eluted at successively decreasing HCl concentrations, the elution order would thus be Th(IV), V(IV), Ti(IV), Hf(IV), Zr(IV), U(IV), Ge(IV), Sn(IV), with Sn(IV) not readily elutable.

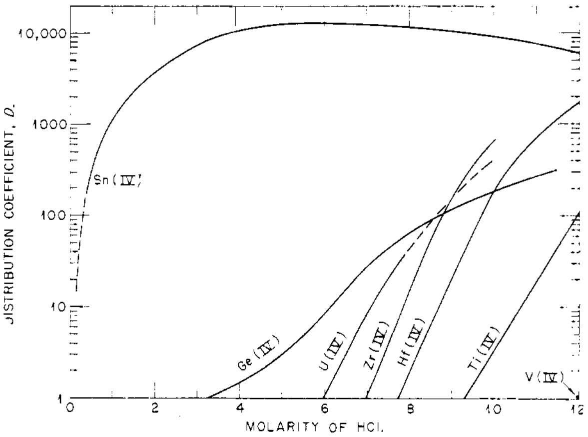

Fig. 1.—Adsorbability of M(IV) ions from HCl solutions.

3. Separations.—The adsorption functions of Th(IV) and U(IV) in HCl solutions are sufficiently different from those of many other elements to imply many useful anion exchange separations. A few typical applications of the data for separations will be discussed.

(a) **Separation of Th(IV) and Pa(V).**—Since Th(IV) shows negligible adsorption from HCl solutions under conditions where Pa(V) shows strong adsorption,[12] these two elements may be separated from each other to any desired degree even at high Th(IV) and low Pa(V) concentrations. Satisfactory separations were achieved, for example, with 1 M ThCl$_4$ solutions in concentrated HCl containing tracer Pa with columns less than 5 cm. long. After the adsorption step, the columns were washed free of Th(IV) with relatively concentrated HCl solutions (preferably M HCl $\geqslant$ 7). Removal of Pa may be achieved at low HCl concentration though care must be taken not to attempt elution at too low an HCl concentration where hydrolysis of Pa might interfere. If presence of fluoride does not cause difficulties, more satisfactory elution of Pa may be achieved with concentrated HCl solutions containing small amounts of HF.[12c]

(b) **Separation of Th(IV), Pa(V) and U(VI).**—The separation of these three elements is based on the facts that Pa(V) and U(VI) can be adsorbed at high HCl concentrations, where Th(IV) is not adsorbed, and that Pa(V) may be eluted with HCl–HF mixtures under conditions where U(VI)

---

[8] A similar divergence in the solution properties of Th(IV) and U(IV) was recently described in connection with the hydrolysis of these ions (K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954)).

[9] K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1460 (1953).

[10] (a) K. A. Kraus, F. Nelson and G. W. Smith *J. Phys. Chem.*, **58**, 11 (1954), (V(IV) and Ti(IV)); (b) F. Nelson and K. A. Kraus, THIS JOURNAL, **77**, 4508 (1955) (Ge(IV)).

[11] E. H. Huffman, G. M. Iddings and R. C. Lilly, *ibid.*, **73**, 4474 (1951).

[12] (a) K. A. Kraus and G. E. Moore, *ibid.*, **72**, 4293 (1950); (b) **73**, 2900 (1951); (c) **77**, 1383 (1955).

remains adsorbed.[13] A typical separation of this type is demonstrated in Fig. 2. For this separation, 0.2 ml. of a solution 0.02 *M* Th(IV) (Th^{230}), tracer Pa^{233} (β,γ, $T_{1/2}$ = 27.4 d), and 0.2 *M* U(VI) in 10 *M* HCl were added to a 0.25 cm.^{2} × 4 cm. column which had been pretreated with 10 *M* HCl. The effluent was analyzed radiometrically for Th(IV) and Pa(V) and polarographically for U(VI). On elution with 10 *M* HCl, Th(IV) was removed in a sharp band free of Pa(V) and U(VI). Elution of Pa(V) was accomplished with 9 *M* HCl–1 *M* HF. U(VI) remained adsorbed at the top of the column and was removed with 0.1 *M* HCl.

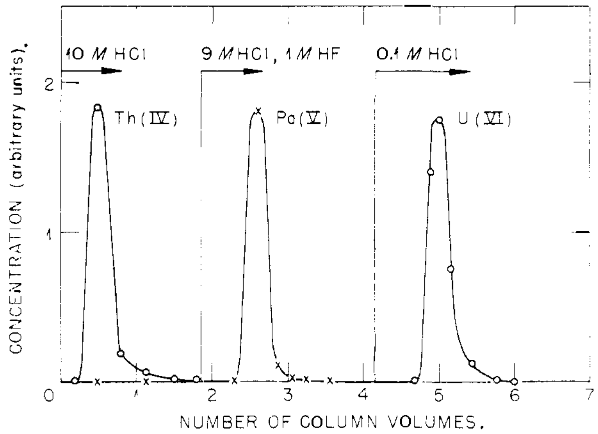

Fig. 2.—Separation of Th(IV), Pa(V) and U(VI).

(c) Separation of U(IV) and U(VI).—U(IV) and U(VI) show sufficient differences in adsorbability from HCl solutions to permit separation from each other by anion exchange. A typical separation (with Th(IV) added) is demonstrated in Fig. 3A. A U(IV)–U(VI) solution was prepared by dissolving in 10 *M* HCl a measured amount of UCl_5 (*ca.* 0.1 *M* U) which through disproportionation gave an equimolar mixture of U(IV) and U(VI). Thorium tracer, (Th^{230}), was added and *ca.* 0.1 ml. of this mixture placed on a 0.25 cm.^{2} × 4.0 cm. column which had been pretreated with 10 *M* HCl. Elution was continued with 10 *M* HCl and the effluent solutions analyzed radiometrically for Th(IV) and polarographically for U(IV) and U(VI). Th(IV) appeared in a sharp band, free from U(IV) and U(VI). U(IV) was eluted in a reasonably sharp band with 3 *M* HCl and U(VI) with 0.1 *M* HCl.

Separation of U(IV) from U(VI) may also be achieved by anion exchange with HCl–HF mixtures. In experiments similar to the one illustrated in Fig. 2, but in which U(VI) was determined radiometrically (U^{233}), it was noticed that a small amount of the alpha activity was found in the HCl–HF fraction containing the bulk of the Pa^{233} activity. Through pulse analyses,[14] the alpha activity was identified as U^{233}. In view of the generally excellent separation of Pa and U(VI), it appeared unlikely that this activity could be due to U(VI) and hence was assumed to arise from a small impurity of U(IV) in the initial tracer. In subsequent experiments it was found that U(IV), in contrast to U(VI), may be eluted readily at high HCl concentrations in the presence of small amounts of HF. A typical separation based on these observations is described in Fig. 3B. For this experiment a typical non-adsorbable element was also added, (Eu(III)), as well as an element which remains strongly adsorbed under conditions where U(IV) and U(VI) are eluted (Zn(II)).[9] An 0.2-ml. aliquot of a solution containing Eu^{155}, 0.003 *M* U(IV) (U^{233}), 0.005 *M* U(VI) (U^{233}) and 0.2 *M* Zn(II) (Zn^{65}) in 8 *M* HCl was added to a 0.17 cm.^{2} × 7.2 cm. column which had previously been pretreated with 8 *M* HCl. On elution with 8 *M* HCl, Eu(III) appeared in a sharp band near 0.4 column volumes as expected. Elution of U(IV) was achieved with 8 *M* HCl–0.1 *M* HF, while U(VI) and Zn(II) were retained. U(VI) was then removed with 0.5 *M* HCl and Zn(II) with 0.01 *M* HCl.

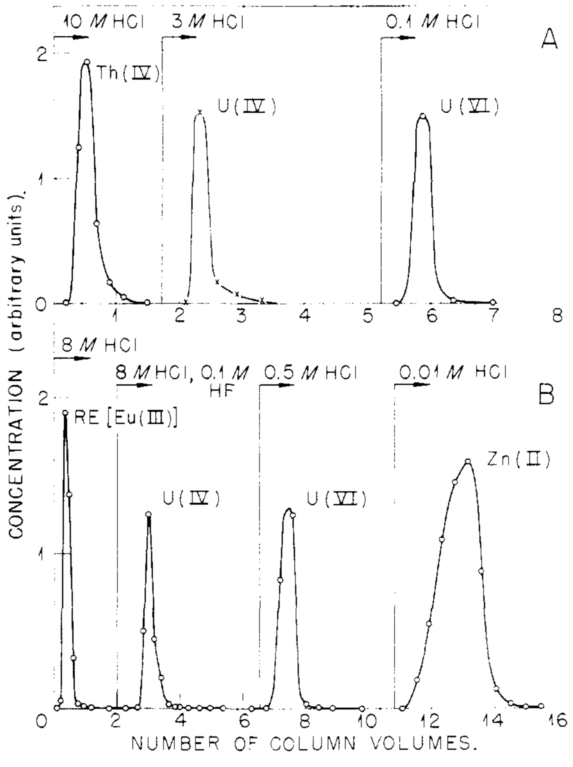

Fig. 3.—Separations involving U(IV) and U(VI).

Intrinsically, these differences in the adsorbabilities of U(IV) and U(VI) may be used for oxidation state analysis. For quantitative results, attempts will presumably have to be made to exclude oxygen from the solutions and columns to prevent errors from air oxidation of U(IV) to U(VI).

---

[13] K. A. Kraus F. Nelson and G. E. Moore, *ibid.*, **77**, 3972 (1955). Separation of Pa(V) and U(V1) can also be achieved with HCl solutions in the absence of HF (K. A. Kraus and G. E. Moore, Report ORNL-330, April, 1949). If elution is carried out at low HCl concentrations, Pa(V) precedes U(VI). For example, on elution with 3.8 *M* HCl, Pa(V) appears in the effluent in maximum concentration at 13 column volumes and U(VI) at 45 column volumes. However, in the absence of HF, the elution bands tend to tail and thus makes separation in HCl solutions less attractive than separations in HCl–HF mixtures.

[14] We are indebted to Mr E. Fairstein of the ORNL Instrument Division for the pulse analyses.

Acknowledgments.—It is a pleasure to thank Miss Donna J. Coombe and Mrs. Hazel Templeton for valuable technical assistance.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A Comparison of the Burning Velocities of Methane and Heavy Methane in Nitrogen and Argon "Airs" at Atmospheric Pressure[1]

BY WILLIAM H. CLINGMAN AND ROBERT N. PEASE

RECEIVED DECEMBER 1, 1955

In order to determine whether diffusion or heat conduction is more important in flame propagation, the burning velocities of methane (CH_4) and heavy methane (CD_4) were measured at atmospheric pressure and in both nitrogen and argon "airs." The Semenov bimolecular equation, based on a thermal theory of flame propagation, predicted a much greater increase in the burning velocity than was observed on going from nitrogen–air to argon–air. The ratio of the burning velocity of a mixture with CH_4 to that of a mixture with CD_4 of the same composition was always greater than one and increased with increasing concentration of fuel. This behavior is in qualitative agreement with a diffusion mechanism. It is shown that a thermal theory does not account for this increase in the burning velocity ratio if it is assumed that changes in the thermal properties of the system such as thermal conductivity, flame temperature, and heat capacity can be neglected upon replacing CH_4 with CD_4.

One of the major unsolved problems in the field of combustion today is the mechanism of flame propagation. Simon[2] has recently reviewed the experimental investigations which have been conducted in order to distinguish between the thermal and diffusion mechanisms of flame propagation. In the former model it is assumed that the conduction of heat from the flame front into the unburned gas is rate controlling while in the diffusion model it is assumed that the rate-controlling steps are the diffusion of active species from the flame front into the unburned gas and subsequent reaction with the fuel. In order to elucidate the relative importance of these two mechanisms the authors[3,4] have measured the burning velocities at reduced pressure of methane–air mixtures in which the nitrogen in the air was substituted with argon or helium. These measured burning velocities were then compared with the Tanford–Pease[5] and Semenov[6] equations of burning velocity based on the diffusion and thermal mechanisms, respectively.

To test further the applicability of these two theories it was proposed that the burning velocities of CH_4 and CD_4 be compared at one atmosphere and varying compositions. Upon replacing the hydrogen atoms in the CH_4 with deuterium atoms only small changes are made in the flame temperature and thermal conductivity of the mixture. The equilibrium atom and radical concentrations are lower in the case of the heavy methane, however, the lower zero point energy of the deuterated compounds compared with the protonated compounds resulting in somewhat decreased dissociation at the flame front into atoms and radicals. The diffusion coefficients for deuterium atoms are also lower than those for hydrogen atoms due to the greater mass of the former. Thus, on the basis of the diffusion mechanism one would expect a decrease in burning velocity on going from CH_4 to CD_4; this decrease would be greater the higher the concentration of deuterium atoms compared to the concentration of the other active species. The burning velocities calculated by a thermal theory, however, will be less dependent on the relative concentration of deuterium atoms at the flame front.

In order to study the effect of isotopic substitution at two appreciably different flame temperatures, measurements of the burning velocity were made over a range of compositions using both nitrogen–air and argon–air.

Experimental

Preparation of CD_4.—The CD_4 was prepared by the decomposition of Al_4C_3 with D_2O following the procedure of Taylor and Wright.[7] The Al_4C_3 and liquid D_2O were refluxed, the temperature of the reactants being equal to the boiling point of the heavy water at the pressure in the system. Carbon dioxide was added to the reaction system in order to keep the pressure at all times above one-half atmosphere and, thus, the temperature of the reactants above about 80°.

The Al_4C_3 was obtained from the Baird Company and was dehydrated by heating *in vacuo* with a flame. The D_2O was obtained from the Stuart Oxygen Company, who listed the isotopic purity as 99.5%. The heavy water was degassed and distilled before use. The CO_2 was obtained from Dry Ice, small amounts of air and water being removed by freezing down in liquid nitrogen, pumping, and subliming about $^5/_6$ of the solid CO_2. This procedure was repeated three times.

The crude product from the decomposition of the Al_4C_3 contained CD_4, CO_2, about 7% D_2,[7] and smaller amounts of higher deuterocarbons. The D_2 was first removed by freezing out the other components of this mixture in a trap surrounded by liquid nitrogen under a pressure of 2–3 cm. (temperature = 57°K.). The bulk of the CO_2 was removed

---

[1] Taken from a thesis submitted by William H. Clingman in partial fulfillment of the requirements for the Ph.D. degree. The work described in this paper was carried out at Princeton University in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and Contract N6ori 105 with the Office of Naval Research and Office of Scientific Research (Air Force) and the Office of Ordnance Research (Army) as coördinated by Project Squid, Princeton University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] D. M. Simon, "Diffusion Processes as Rate-Controlling Steps in Laminar Flame Propagation," Colloquium held by the Advisory Group for Aeronautical Research and Development, North Atlantic Treaty Organization, at Cambridge, England, December 7–11, 1953.

[3] W. H. Clingman and R. N. Pease, to be published.

[4] W. H. Clingman, R. S. Brokaw and R. N. Pease, "Fourth Symposium on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1953, pp. 310–313.

[5] C. Tanford and R. N. Pease, *J. Chem. Phys.*, **15**, 861 (1947).

[6] N. N. Semenov, *Prog. Phys. Sci.* (*USSR*), **24**, No. 4 (1940). Translation appears as N.A.C.A. TM No. 1026, 1942.

[7] M. M. Wright and H. S. Taylor, *Can. J. Research*, **27B**, 303 (1949).