[CONTRIBUTION FROM THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Equilibrium Sorption of Lanthanides, Americium and Curium on Dowex-50 Resin

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The equilibrium sorption of the tripositive lanthanides and americium and curium from 0.110 m perchloric acid solutions on Dowex-50 cation-exchange resin has been studied at 25°. The relative sorbability decreased from lanthanum to dysprosium. From dysprosium to lutetium almost no change in sorbability was observed. Americium and curium sorbed with the same strength as lanthanides of comparable crystallographic radius. A correlation of ion-exchange sorbabilities and ionic conductance at infinite dilution has been made. By studying the effect of temperature on sorption of americium, promethium, thulium and lutetium heats and entropies were obtained. The reaction was found to have a considerable ΔC_p effect. Thermodynamic quantities calculated for americium and promethium differed from those of thulium and lutetium.

Introduction

A considerable amount of work has been done on the ion-exchange elution behavior of actinides and lanthanides. Elution of actinides and lanthanides from cation-exchange resins has been studied using ammonium citrate,[1-5] ammonium lactate,[5-9] ammonium α-hydroxy isobutyrate,[10,11] ammonium thiocyanate,[12] and hydrochloric acid[5,13,14] as eluants. With the exception of concentrated hydrochloric acid eluent, the order of appearance of the ion in the effluent solution is the inverse order of atomic number, which is also taken to be the order of decreasing radius of the hydrated ion. Except for ammonium thiocyanate and concentrated hydrochloric acid eluents, actinides elute near lanthanides of comparable ionic radii; *i.e.*, americium elutes near promethium. In all of these systems studied considerable complex ion formation occurs between the actinide or lanthanide ion and the eluent. It has been pointed out that a number of factors can affect the elution position of an ion, such as radius of the hydrated ion and extent and type of complex ion formation.[5] The equations for the ion-exchange reaction may be written as

$$M^{+3} + 3R^- = MR_3 \qquad (1)$$

for the sorption of the tripositive ion on the resin and

$$M^{+3} + yA^{-x} = MA_y^{3-yx} \qquad (2)$$

for the formation of the complex ion, where M^{+3} is the tripositive actinide or lanthanide ion, R^- is the immobile resin anion and A^{-x} is the complexing eluent anion. It is the purpose of the present work to study the reaction represented by equation 1 for the lanthanides and americium and curium.

Experimental

In order to minimize complex ion formation, it was decided to measure the distribution of tracer amounts of the ions studied between a low ionic strength perchloric acid solution and hydrogen form Dowex-50 resin. There are several reasons for choosing this experimental method: (1) batch equilibrations are more accurate than elution from an ion-exchange column; (2) elution from an ion-exchange column would not be practical using low ionic strength noncomplexing eluent, because of the high affinity of tripositive ions for Dowex-50 resin; (3) the use of tracer concentrations simplifies thermodynamic calculations.

Materials.—The Dowex-50 4% cross-linked resin was prepared from a single large batch of 200–400 mesh by a "wet grading" method. That fraction having a settling rate in water of 0.5–1 cm. min.$^{-1}$ was used. The mean diameter of the dry resin particles was 29 μ. Following the grading, the resin was purified by alternate washes with strong and weak hydrochloric acid, NH_4OH, $HClO_4$, NaOH and conductivity water. The resin was left in the hydrogen form and dried in an oven at 110° to constant weight. Titration with NaOH showed the mole equivalent weight of the resin to be 199.

$HClO_4$ solutions were prepared from pure concentrated (72%) $HClO_4$ and conductivity water (specific conductance 0.7 to 2×10^{-7} mho).

The radioactive tracers employed were La^{140}, Ce^{144}, Pr^{142}, Nd^{147}, Pm^{147}, Sm^{153}, $Eu^{154,155}$, $Gd^{153,159}$, Tb^{160}, Dy^{165}, Ho^{166}, $Er^{169,171}$, Tm^{170}, $Yb^{169,175}$, Lu^{177}, Am^{241} and Cm^{242}. The cerium, promethium and europium activities were obtained from the Oak Ridge National Laboratory. Americium and curium had been produced by neutron irradiation of Pu^{239}. The remaining activities were produced by neutron irradiation of microgram amounts of the stable isotopes in the Materials Testing Reactor (Arco, Idaho), with the exception of Dy^{165} which was produced in the Livermore reactor (University of California Radiation Laboratory, Livermore, California).

Method.—Following irradiation, the activities were purified by a Dowex-50 ion-exchange column utilizing ammonium α-hydroxyisobutyrate as eluent.[11] Identification of the activity following separation was made either by a previous knowledge of its elution peak position or by its characteristic nuclear properties; *i.e.*, half-life or maximum β^- energy.

A stock solution containing the desired amount of tracer activity in 0.110 *M* $HClO_4$ was prepared and analyzed radiometrically and for hydrogen ion. A known amount (usually 10 ml.) of the stock solution was introduced into a glass-stoppered flask containing an accurately weighed amount (2–4 mg.) of Dowex-50 resin. The resin was weighed on an Ainsworth Model VM assay balance. Corrections were applied to obtain the weight *in vacuo*. It was estimated that the probable error in weight did not exceed 6 μgrams.

The flask was then sealed and rotated in a thermostated bath, usually for 24 hours, although equilibrium was obtained in less than 4 hours. Aliquots of the equilibrated solution were then removed from the flask for radiometric assay. Counting was performed with a windowless proportional counter, except for americium and curium which were counted in a 2π geometry α-particle counter. The distribution coefficient, K_d, was then calculated as

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$$K_d = \frac{\text{counts/min. per gram resin}}{\text{counts/min. per ml. soln.}}$$

If the hydrogen ion concentration of the equilibrating solution was different from 0.1100 M, a correction was applied to the measured K_d to obtain the distribution coefficient in 0.1100 M hydrogen ion, denoted as K_{d_0}.

Because of the small amount of resin used, polyvalent cationic impurities must be at a low level in these experiments. Some typical spectrographic analyses are shown in Table I, indicating the amount and source of impurities. The mass of stable isotopes present in a single experiment varied from 6 μg. for europium to 0.003 μg. for terbium.

TABLE I

SPECTROGRAPHIC ANALYSIS

Sample	Impurity (μg.) Al	Ca	Fe	Mg
0.110 M HClO$_4$ (10 ml.)	ND[a]	0.1	ND	0.1
Dowex-50 (1 mg.)	ND	ND	ND	ND
Cerium tracer	0.05	0.3	ND	0.02
Neodymium tracer	0.05	0.05	0.05	0.03

[a] ND signifies that the impurity is below the level of sensitivity for detection (0.01 μg.).

Results

Sorption of Lanthanides, Americium and Curium at 25°.—In Table II the results of the measurements on the lanthanides and americium and curium are given in terms of K_{d_0}. Several of the determinations on a single ion (cerium, promethium, europium, thulium, lutetium and americium) were performed twice, using different amounts or different sources of tracer and at widely spaced time intervals. The difference in the average K_{d_0}'s from separate experiments amounted to slightly over 3% in the worst case.

The logarithm of the average K_{d_0} from Table II is plotted against the crystallographic radius of the ion in Fig. 1. The crystallographic radii of lanthanides are those given by Templeton.[15] The radius of americium is taken to be 1.00 Å.[16] and that of curium as 0.99 Å.[17] For the lanthanides a curve with the same slope would be obtained by plotting against atomic number rather than crystallographic radius.

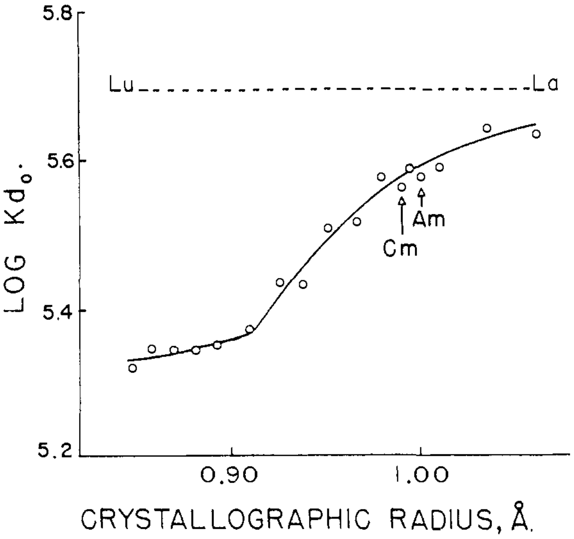

Fig. 1.—Logarithm of K_{d_0} *vs.* the crystallographic radius for lanthanides, americium and curium.

Sorption of Promethium, Thulium, Lutetium and Americium at 0 and 50°.—For the purpose of determining heats and entropies of sorption, experiments were performed with promethium, thulium, lutetium and americium at 0 and 50°. The results of the experiments are shown in Table III.

The equation for the reaction may be written as

$$M^{+3} + 3HR = MR_3 + 3H^+ \quad (3)$$

$$K = \frac{(MR_3)(H^+)^3}{(HR)^3(M^{+3})} = \frac{[MR_3][H^+]}{[HR]^3[M^{+3}]} = \frac{\gamma_{MR}\gamma^3_{H^+}}{\gamma^3_{HR}\gamma_{M^{+3}}} \quad (3a)$$

where M^{+3} is the tracer ion, R the resin anion and γ is the activity coefficient in the phase indicated. Since HR does not change when tracer concentrations are employed, $(HR)^3$ is unity. The resin phase activity coefficients are not known and will arbitrarily be set equal to unity.

$$K' = \frac{[MR_3][H^+]^3\gamma^3_{H^+}}{[M^{+3}]\gamma_{M^{+3}}} = cK_{d0}\frac{[H^+]^3\gamma^3_{H^+}}{\gamma_{M^{+3}}} \quad (4)$$

where "c" is a constant of proportionality to transform K_{d_0} to a molal-equivalent basis. Its value is 0.199. K' is not a strict thermodynamic constant because of the neglect of the resin phase activity coefficients. $[H^+]$ is now fixed to the value at which K_{d_0} was determined. Then

$$-\Delta F° = RT \ln K' = 4.57T \log 0.199K_{d_0}\frac{(H^+)^3\gamma^3_{H^+}}{\gamma_{M^{+3}}} \quad (5)$$

The work of Spedding and co-workers[18] shows that the activity coefficients of the lanthanide chlorides have the same value at a given μ (ionic strength) up to a μ of 0.2 at least. Since this experiment μ was 0.11, it is assumed that $\gamma_{M^{+3}}$ will be the same for all M^{+3} ions. As all M^{+3} ions are in tracer concentration the γ_{H^+} will be that of the pure solution. For the evaluation of the activity coefficients the compilation of Kielland[19] for the individual ion was used. A correction for the variation of activity coefficient with temperature was applied.[20] Finally

$$-\Delta F° = 4.57T \log \alpha K_{d_0} \times 10^{-4} \quad (6)$$

where α has the value 6.73, 7.00 and 7.42 at 0, 25 and 50°, respectively. Because the elevated temperature was not exactly 50° a linear correction in γ was made.

For calculating $\Delta H°$ and $\Delta S°$ the following relationships[21] were used

$$\Delta F° = \Delta H° - \Delta C_p T \ln T + IT \quad (7)$$

and

$$\Delta H° = \Delta H_0° + \Delta C_p T \quad (8)$$

where ΔH_0, ΔC_p and I are constants which may be evaluated by solving 7 as a simultaneous set of

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equations using the values of ΔF° calculated by 6. Once the constants are evaluated, equation 8 may be used to calculate the ΔH° of the reaction. The ΔS° may then be calculated through the relationship

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (9)$$

where ΔS° is the entropy change.

The constants in the equation for each ion that result from solving 7 are given in Table IV. The thermodynamic quantities obtained by solving equations 6, 8 and 9 are also given.

TABLE II

SORPTION OF TRIPOSITIVE LANTHANIDES, AMERICIUM AND CURIUM

The solution volume was 10 ml. The initial concentration in counts/minute of tracer per milliliter is C_0 and the final concentration, C_s. Temperature was 24.98 ± 0.03°.

Ion	$HClO_4$ concn. (M)	Resin wt. (mg.)	$C_0 \times 10^{-5}$	$C_s \times 10^{-3}$	$K_{d_0} \times 10^{-5}$
La	0.1110	1.610	0.574	0.851	4.28
	.1110	1.875	0.561	.704	4.33
Ce	.1102	2.742	1.002	.810	4.49
[a]	.1102	2.192	1.017	1.021	4.52
[a]	.1115	2.668	3.182	1.584	4.38
[a]	.1115	1.557	3.182	2.226	4.40
	.1099	2.539	3.346	2.960	4.40
	.1099	3.112	3.346	2.471	4.31
Pr	.1110	2.843	5.344	4.979	3.84
	.1110	3.048	5.302	4.532	3.91
Nd	.1112	1.632	0.472	0.787	3.73
	.1112	1.481	0.468	0.839	3.82
Pm	.1102	3.179	1.005	0.848	3.72
	.1102	2.416	1.005	1.089	3.80
	.1099	3.809	3.382	3.294	3.83
	.1099	3.906	3.382	2.207	3.89
	.1099	1.429	3.382	6.326	3.66
Sm	.1110	2.375	2.112	2.762	3.26
	.1110	2.058	2.086	3.135	3.27
	.1110	2.883	2.059	2.184	3.32
Eu	.1102	1.844	0.653	1.108	3.16
	.1102	2.379	0.653	0.815	3.35
	.1099	2.460	5.026	6.488	3.10
	.1099	4.117	5.004	3.605	3.34
	.1099	3.463	5.004	4.472	3.19
Gd	.1110	2.336	7.99	12.95	2.70
	.1110	2.824	7.90	10.28	2.75
Tb	.1102	2.310	0.255	0.395	2.76
	.1102	4.242	0.255	0.220	2.72
Dy	.1110	1.732	1.126	2.740	2.38
	.1110	2.618	0.842	1.361	2.39
	.1110	2.250	0.684	1.309	2.34
Ho	.1110	2.016	5.160	11.64	2.21
	.1110	2.420	5.104	9.38	2.27
	.1110	2.162	5.046	10.34	2.27
Er	.1110	2.661	1.637	2.770	2.23
	.1110	1.400	1.614	5.234	2.18
Tm	.1112	2.634	1.384	1.202	2.23
	.1112	2.603	1.358	2.332	2.27
	.1112	1.862	1.358	3.330	2.19
	.1098	1.758	4.280	10.82	2.21
	.1098	2.985	4.270	6.37	2.20
Yb	.1108	1.982	0.600	1.375	2.21
	.1108	2.542	0.600	1.052	2.24
Lu	.1112	1.643	1.180	3.488	2.08
	.1112	2.606	1.180	2.130	2.15
	.1098	1.982	0.568	1.347	2.03
	.1098	2.451	0.460	0.879	2.08
Am	.1102	1.945	1.747	2.350	3.78
[a]	.1102	2.435	1.747	1.868	3.81
[b]	.1102	2.346	1.747	0.580	3.85
	.1100	2.319	4.115	4.498	3.80
	.1100	2.098	4.115	5.023	3.78
	.1100	2.188	4.115	4.783	3.81
Cm	.1102	2.592	0.475	0.496	3.65
[a]	.1102	1.844	0.475	0.357	3.57
[b]	.1102	1.451	0.475	0.269	3.62

[a] 5-ml. solution. [b] 3-ml. solution, measured in Teflon container.

TABLE III

SORPTION AT 50 AND 0°

Symbols have the same meaning as in Table II

Ion	$HClO_4$ concn. (M)	Temp. (°C.)	Resin wt. (mg.)	$C_0 \times 10^{-5}$	$C_s \times 10^{-3}$	$K_{d_0} \times 10^{-5}$
Lu	0.1097	0.00	1.982	0.338	0.851	1.94
	.1098	.00	2.451	.307	.617	1.97
[a]	.1013	.00	2.377	.374	.603	2.01
	.1097	49.53	2.329	.719	1.194	2.52
	.1098	49.53	2.377	.656	1.098	2.46
	.1098	49.53	2.507	.634	0.996	2.49
	.1098	49.53	2.451	.591	0.964	2.45
Tm	.1096	0.00	2.116	4.234	9.340	2.08
	.1097	.00	1.758	4.192	11.400	2.02
	.1098	.00	2.985	4.186	6.780	2.02
	.1098	49.53	3.217	4.380	4.951	2.71
	.1098	49.53	2.116	4.360	7.514	2.69
	.1098	49.53	2.686	4.360	6.027	2.65
	.1098	49.53	2.985	5.367	2.68	2.66
Pm	.1099	0.00	3.809	3.330	2.218	3.88
	.1099	0.00	3.906	3.300	2.144	3.80
	.1099	48.20	3.809	3.274	1.976	4.28
	.1099	48.20	3.906	3.274	1.890	4.34
Am	.1100	0.00	2.098	4.115	4.963	3.91
	.1098	0.00	2.188	4.115	4.800	3.84
	.1100	48.20	2.098	4.115	4.460	4.34
	.1100	48.20	2.188	4.115	4.228	4.36
	.1100	48.20	2.319	4.115	4.047	4.31

[a] Some leakage from the bath water into the equilibration vessel occurred.

Table IV is somewhat misleading in that no error limit has been set on the values. The accuracy of ΔH° is dependent ultimately on the accuracy with which the ΔF° can be measured. If one assumes a probable error of 1% in K_{d_0}, then the probable error in evaluating ΔC_p is approximately 17%. Now this error is compensated for in equation 7 because in this case "I" is determined almost entirely by the value of ΔC_p. Thus the relative value of ΔH_0 will also be quite good. In evaluating ΔH° by equation 8 the inherent error in ΔC_p is not entirely compensated for; but even for a large error in K_{d_0}, the ΔH° should not be in

TABLE IV

FREE ENERGY, HEAT AND ENTROPY OF SORPTION

Ion	Constants of eq. 8			$-\Delta F^\circ_{298}$ (kcal.)	ΔH°_{298} (kcal.)	ΔS°_{298} (e.u.)
	$-\Delta H_0$	ΔC_p	I			
Lu	12098	44.71	285.5	2.951	1.24	14.0
Tm	11495	43.27	275.1	2.986	1.41	14.7
Pm	15412	54.63	352.0	3.302	0.88	14.0
Am	16012	56.58	365.1	3.305	0.86	14.0

error by more than 10%. The error in ΔS° is more dependent on the error in ΔF° than in ΔH°. A reasonable estimate of the error in ΔS° would be less than 5%.

Discussion

It has long been recognized that ion exchange of strong electrolytes is governed by the charge and hydrated radii of the exchange ions.[22–24] Semi-quantitative correlations have been made between sorbability of ions and hydrated radii obtained from ion mobilities (Stokes' law calculations[23]) and by taking the Debye–Hückel parameter, $\mathring{a}$, as an index of hydrated ionic radii.[24] The expected dependence is[24]

$$-\Delta F^\circ \propto 1/\mathring{a} \qquad (10)$$

In the case of the lanthanides, the $\mathring{a}$ values which are known are not accurate enough to provide a comparison with the sorbabilities obtained in this work. Qualitatively, however, the hydrated radii of lanthanides should be the inverse of the crystallographic radii. Equation 6 shows that log K_{d_0} is proportional to $-\Delta F^\circ$. Figure 1 then is essentially a plot of equation 6, assuming the crystallographic radius is inversely proportional to the hydrated radius. In general, the trend for the lanthanides is as expected. Americium and curium sorb to the same extent as lanthanides of comparable crystallographic radii. This indicates that no large difference in sorption is caused by the different electronic configurations of actinides compared to lanthanides.

The conductances at infinite dilution have been obtained for a number of lanthanide chlorides, bromides, and perchlorates.[25–29] Ionic conductances of lanthanide ions have been calculated from those data using the values of 76.34, 78.4 and 68.0 for chloride, bromide and perchlorate ions, respectively.[30] The results are listed in Table V. Also included are the calculated standard free energies of formation of metal resinate from the data of Table II. The ionic conductance is one index of the degree of hydration of an ion. For similarly charged ions, the ionic conductance is larger for the ion of smaller hydrated ionic radius. Assuming the conductance to be inversely proportional to the hydrated ionic radius, a plot of ionic conductance *vs.* $-\Delta F^\circ_{298}$ should be linear, comparing similarly charged ions. Figure 2 is such a plot for lanthanides. Considering the possible errors involved, the agreement is excellent.

If the assumptions made were strictly true, the ratio of ionic conductance at infinite dilution to negative free energy of formation of metal resinate should be a constant. Actually the ratio decreases 7% in a regular fashion from lanthanum to about dysprosium or holmium. Dysprosium, holmium, erbium, thulium and ytterbium give ratios which vary less than 2%, which is approximately the error range expected for the combined measurements.

TABLE V

FREE ENERGIES OF FORMATION OF METAL RESINATE AND IONIC CONDUCTANCE AT INFINITE DILUTION

Ion	$-\Delta F^\circ_{298}$ formation of metal resinate	Ionic conductance at infinite dilution[a]
La	3.38	69.3
Ce	3.39	69.9
Pr	3.31	69.2
Nd	3.30	69.5
Pm	3.30	
Sm	3.22	68.2
Eu	3.20	67.9
Gd	3.11	67.0
Tb	3.11	
Dy	3.02	65.7
Ho	3.00	66.0
Er	2.98	65.8
Tm	2.99	65.5
Yb	2.99	65.4
Lu	2.95	
Am	3.30	
Cm	3.27	

[a] Calculated from the data of references 25, 26, 27, 28 and 29.

Notice that the curve in Fig. 1 has a peculiar shape. From lanthanum to dysprosium a gradual decrease in sorbability occurs, but from dysprosium to lutetium there is almost no change in sorbability. The equation for the reaction studied can be

$$M(H_2O)_a^{+3} + 3H(H_2O)_bR = M(H_2O)_cR_3 + 3H(H_2O)_d + (a + b - c - d)H_2O \qquad (11)$$

taking into account the decrease in hydration of the ion when it is sorbed on the resin. If a change in the average number of hydration waters occurred in the neighborhood of dysprosium, such a curve might result. The lanthanides heavier than dysprosium, having fewer waters of hydration than the lighter lanthanides, would appear to sorb too strongly on a relative basis. This discontinuity in the neighborhood of dysprosium (actually the discontinuity occurs between terbium and dysprosium) can also be observed in the ΔF° and ΔH° of M^{+3}(aq.), the ΔH° of MCl_3(aq.), and in the ΔF° of $M(OH)_3$, $M_2(SO_4)_3 \cdot 8H_2O$[24] (where M^{+3} is the lanthanide ion), and in the ionic conductances, if those quantities are plotted against the crystallographic radii of the ions.

It should be pointed out, however, that the thermodynamic quantities cited above depend to a large degree on measurements made on the metals.[31] Thus an error in the measurements on the metals would be reflected in the above values. Also, the crystallographic radii exhibit a slight discontinuity (with atomic number) between gadolinium and terbium. Ion-exchange elution positions (which are proportional to sorbabilities) of

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(31) H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 357 (1941).

lanthanides from Dowex-50 resin columns indicate a discontinuity (with atomic number) between gadolinium and terbium with eluting agents such as ammonium lactate.[5] This, of course, could be a result of complex-ion formation rather than sorption on the resin.

There is one objection in the method used here for the evaluation of ΔS°. In deriving equation 9, one of the implied assumptions was that a reference state was chosen in which all M(III) ions would have the same thermodynamic activity, *i.e.*, a resin phase which is essentially all in the hydrogen form. This means that the resin phase activity coefficients are identical for different M(III) ions. The resin phase may be thought of as a concentrated ionic solution having an ionic strength of approximately 2.5. (The hydrogen form resin has a capacity of 5 equivalents per 1000 g. of dry resin, and water absorption increases the volume by a factor of two.) It could hardly be expected that the M(III) ions would all have the same activity coefficients. It is possible to make a crude guess as to how much difference there would be in the activity coefficients. The activity coefficients of aqueous $NdCl_3$ and YCl_3 at an ionic strength of 2.4 are 0.289 and 0.309.[32] Assuming that this ratio is the same as the ratio of resin phase activity coefficients, and that the activity coefficient of neodynium is the same as those of americium and promethium and that of yttrium is the same as those of thulium and lutetium, a difference in ΔF°_{298} of 0.043 kcal. could be expected. This amounts to an error of 2% in the relative value of ΔF°, which would also appear in ΔS° but not in ΔH°.

It is fortuitous that the $\Delta S^{\circ\prime}$s of americium, promethium, thulium and lutetium are the same within experimental error at 25°. At 0° the difference in $\Delta S^{\circ\prime}$s of americium and promethium from those of thulium and lutetium amounts to 1 e.u. This is a consequence of the apparently different ΔC_p's. While these data are not extensive enough or precise enough to say that this is a real effect, it is certainly a strong indication, especially since the ΔC_p's of both americium and promethium are approximately 55 while both lutetium and thulium are approximately 44. This might be interpreted as evidence that a different amount of coördinated water is lost on sorption of the heavy lanthanides with respect to the amount lost by the light lanthanides.

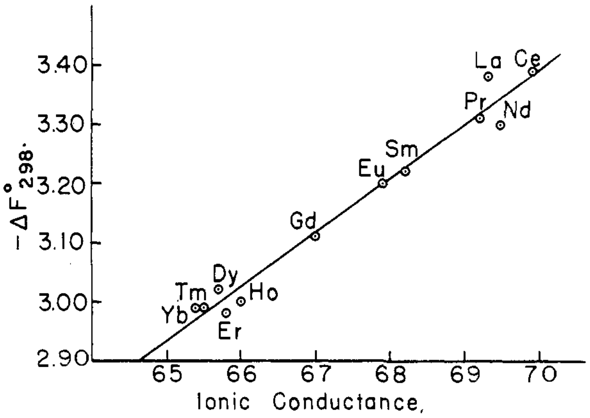

Fig. 2.—Free energy of formation of metal resinate *vs.* ionic conductance at infinite dilution for some lanthanides.

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(32) C. M. Mason, THIS JOURNAL, **63**, 220 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Crystal Structure of Arsenomethane

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The yellow form of arsenomethane crystallizes with a monoclinic unit cell of dimensions a = 8.89 Å., b = 12.54 Å., c = 11.55 Å., and $\beta = 101°46'$. The space group is $C^5_{2h} - P2_1/n$. The arsenic atoms of one molecule are joined in a puckered, five-membered ring; to each arsenic atom is bonded one methyl group. The As–As bond distances vary from 2.42 to 2.44 Å. with an average of 2.428 Å.; the average value of the As–C bond length is 1.95 Å. The As–As–As bond angles have values from 97½° to 105½°, while the average of the C–As–As bond angles is about 97°.

Arsenomethane exists in two forms at room temperature: a yellow oil (m.p. 12°) and a red solid. Both forms were investigated by Waser and Schomaker[1] who used vapor density measurements and electron diffraction of the vapor to study the oil and X-ray powder pictures to investigate the solid. A conclusive structure for the molecule was not obtained, although a puckered five-membered ring of As atoms with an As–As–As bond angle of about 90° appeared to explain their data for the yellow form in a natural way.

In this paper will be described a low temperature, single crystal, X-ray diffraction study of the yellow modification by which its crystal structure was determined.

Experimental Procedure

The yellow form of arsenomethane was obtained by reducing sodium methyl arsonate with hypophosphorous acid. Single crystals were grown and maintained in Pyrex capillaries by cooling with a stream of cold air. Both precession and Weissenberg cameras were employed, the latter being modified in a fashion similar to that described by Collin and Lipscomb[2] to accommodate the cooling apparatus.

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(1) J. Waser and V. Schomaker, THIS JOURNAL, **67**, 2014 (1945).

(2) R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 10 (1951).