

TABLE IV
 K_{sp}^0 FOR $CsIO_4$

Temp, °C	K_{sp}^0
5	$(3.96 \pm 0.17) \times 10^{-4}$
25	$(2.24 \pm 0.07) \times 10^{-3}$
40	$(6.53 \pm 0.04) \times 10^{-3}$

coefficients f_1 and f_2 can be calculated from the Davies equation¹⁹

$$-\log f_i = Az_i^2[(\mu^{1/2}/(1 + \mu^{1/2})) - 0.3\mu] \quad (12)$$

where μ is the ionic strength in moles per liter, z_i is the charge on the i th type of ion, and A is a constant for a given temperature in water.²⁰

A graph was made of $-\log K_{sp}^0$ vs. $(1/T) \times 10^3$ which included a point for 60° calculated from a single determination of the solubility at that temperature. From this plot, ΔH_{soln}^0 was calculated to be 13.1 kcal/mole. ΔG_{soln}^0 at 25° was calculated to be 1.91 ± 0.05 kcal/mole, and ΔS_{soln}^0 was calculated to be 37.6 eu.

Table III also indicates the solubilities calculated using the values of K_{sp}^0 found. It is seen that the values of K_{sp}^0 employed adequately explain the experimental data.

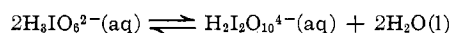
Solubility studies at higher pH values than those reported were not feasible because of the precipitation of periodates of the cation of the inert electrolyte.

(19) C. W. Davies, "Ion Association," Butterworth and Co. Ltd., London, 1962, p 41.

(20) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, revised, Butterworths and Co. Ltd., London, 1965, p 468.

For example, when $NaNO_3$ - $NaOH$ mixtures were used to obtain initial pH values in the range 10-13, a solid of high sodium content (probably $Na_2H_3IO_6$) separated from solution as a consequence of the higher concentration of doubly and triply charged periodate anions in the more basic solutions. After a literature search and several exploratory experiments, it was found that a suitable ionic medium could not be found to extend the pH range above about 6. Previous studies in basic solution^{2,5} were either done at a single pH or employed periodates of such low solubilities that concentrations of the various periodate species were never high enough to cause precipitation of the cations added to maintain constant ionic strength.

In order to explain the formation of salts of the anion $H_2I_2O_{10}^{4-}$, a dimerization equilibrium has been postulated at high pH²¹



$$K_{dim}^0 = \frac{(H_2I_2O_{10}^{4-})f_4^2}{(H_3IO_6^{2-})^2f_2^2} = 2400 \text{ at } 1.0^\circ, 600 \text{ at } 25.0^\circ \quad (13)$$

This anion is probably present in the salt $Cs_4H_2I_2O_{10} \cdot 8H_2O$, which we have prepared and reported in the Experimental Section. The inclusion of this dimerization equilibrium in the calculations of the solubility of $CsIO_4$ is of no importance in evaluating K_{sp}^0 from the data obtained in this study, because even at the highest pH studied, the concentration of dimer in solution is not significant.

(21) G. J. Buist and J. D. Lewis, *Chem. Commun.*, 86 (1965).

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Thermodynamic Studies in the Polyiodide Systems RbI - RbI_3 , NH_4I - NH_4I_3 , CsI - CsI_3 , and CsI_3 - CsI_4

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The free energy of the reaction $MI(s) + I_2(s) = MI_3(s)$ for the polyiodide systems RbI - RbI_3 , NH_4I - NH_4I_3 , and CsI - CsI_3 and of the reaction $CsI_3(s) + \frac{1}{2}I_2(s) = CsI_4(s)$ was determined from emf measurements of solid-state cells of the types $Ag|AgI|C$, MI - MI_3 (or C , CsI_3 - CsI_4) and $Ag|AgI|C$, $I_2(s)$. For the temperature range 25-113.5° ΔG° values (kcal/mole) of the above reactions are given by $\Delta G^\circ = -2.48 + 2.30 \times 10^{-3}(T - 273)$ for RbI - RbI_3 , $\Delta G^\circ = -1.78 + 1.10 \times 10^{-3}(T - 273)$ for NH_4I - NH_4I_3 , $\Delta G^\circ = -3.48 + 0.92 \times 10^{-3}(T - 273)$ for CsI - CsI_3 , and $\Delta G^\circ = -0.64 + 0.57 \times 10^{-3}(T - 273)$ for CsI_3 - CsI_4 . From these free energies and the vapor pressure of solid iodine, dissociation pressure expressions for the polyiodides were found for the same temperature range. The standard entropies, free energies, and heats of formation as well as the aqueous heats of solution of the polyiodides at 25° were calculated.

Introduction

Although the existence of polyiodides of ammonium, as well as of the alkali metals cesium and rubidium, has long been known, the only thermodynamic measurements reported on these systems have been those of Foote, *et al.*,¹⁻³ and Stepin, Babkov, and Sas.⁴ To

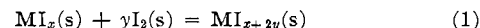
(1) H. W. Foote and W. M. Bradley, *J. Phys. Chem.*, **37**, 29 (1933).

(2) H. W. Foote, W. M. Bradley, and M. Fleischer, *ibid.*, **37**, 21 (1933).

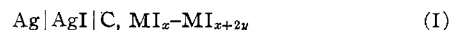
(3) H. W. Foote and M. Fleischer, *ibid.*, **44**, 633 (1940).

(4) B. D. Stepin, A. V. Babkov, and T. M. Sas, *Zh. Neorgan. Khim.*, **10**, 1603 (1965).

obtain thermodynamic data for the reaction



an emf study was undertaken on cells of the types



where MI_x - MI_{x+2y} represents the NH_4I - NH_4I_3 , RbI - RbI_3 , CsI - CsI_3 , and CsI_3 - CsI_4 systems and $I_2(s)$ elemental iodine.

Experimental Section

The ammonium iodide and silver iodide were the best grades available from Mallinckrodt. The rubidium iodide (99.9%) and cesium iodide (99.5%) were obtained from Research Inorganic Chemical Co. (Sun Valley, Calif.). These salts were used without further purification. The polyiodides were prepared by allowing the monoiodides to react with stoichiometric quantities of reagent grade iodine at 65° in evacuated, sealed vessels for 1 week.

The emf's of the cells were measured with a Rubicon potentiometer, Model 2781, and a Hewlett-Packard dc microvolt-ammeter, set at 1-mv full scale, as the null detector. Each pair of half-cells, Figure 1, was made from 0.71- and 0.94-in. diameter 10-ml hypodermic syringes, with the closed ends of the outer barrels cut off. The larger syringe (10) with its open end ground flat served as the iodine electrode and contained a 0.75-in. diameter closed, porous-faced graphite cup (5) with the polyiodide-iodide mixture or elemental iodine. Thus no contact between the AgI (4) and the iodide or iodine occurred except through the gas phase, and this eliminated the occurrence of reaction between the AgI and the iodide salt. The smaller syringe (9) had its open end flared and ground flat and contained a 0.5-in. diameter silver electrode pellet (3). For the iodine electrodes pure iodine, 70:30 mixtures by weight of the triiodide and monoiodide, or approximately 50:50 mixtures of CsI₄ and CsI₃ were used. The silver electrode consisted of powdered silver pelletized with silver iodide and carbon. These electrodes yielded emf's which agreed with each other to ±0.2 mv for the temperature range of measurement, 25–150°. Tungsten wire (0.040-in. diameter) (1) was sealed through the plunger and joined to a graphite disk (2) at the inner face of the plunger. These served as electrical leads in all of the half-cells and eliminated thermoelectric potential corrections. The silver iodide pressed pellet (4) was 1 in. in diameter and about 1/16 in. thick. When the cell was assembled the AgI disk, butted up against the flat-ground edges of the syringe barrels, protruded beyond the cell walls and prevented direct contact of iodine vapor with the silver. The half-cells were held together and contact was achieved among the graphite disk leads, electrodes, and AgI by means of brass rings (7) with spring loads (8) on the outside of the cells. The cells were then placed in Pyrex tubes which could be evacuated and through which argon could flow. The argon was allowed to pass down the tubes from the silver to the iodine side to minimize further the presence of iodine vapor in the silver half-cell. The tubes, in turn, were enclosed in 1/8-in. wall copper tubing to minimize temperature gradients and fluctuations. The cell assembly was heated in a vacuum oven containing a gas manifold and lead-through seals. All measurements were made in an argon atmosphere at approximately 10° intervals over a temperature range from 25 to 150° with both ascending and descending temperatures. The temperatures were monitored with thermometers inserted between the copper and Pyrex tubes enclosing the cells.

In general, constant and reproducible potentials were found with ascending temperatures within 2 hr after the temperature had become constant. With descending temperatures, however, much longer times were required before reproducible emf's were obtained; in fact, at the lower temperatures constant emf's were frequently not attained in systems of low iodine pressure even after 2 days. Since with solid iodine as well as many of the polyiodide cells reproducible potentials were found at both ascending and descending temperatures, although again with the latter at longer times, it appears likely that desorption of iodine from the graphite may be slow. In addition, the recombination of iodine vapor with the solid salts may be diffusion or kinetically limited. Thus in those cases where the agreement between the potentials found with ascending and descending temperatures was poor, *i.e.*, for differences greater than 2 mv, only the values measured with increasing temperature were taken.

Results

The reaction measured by cells of type I is

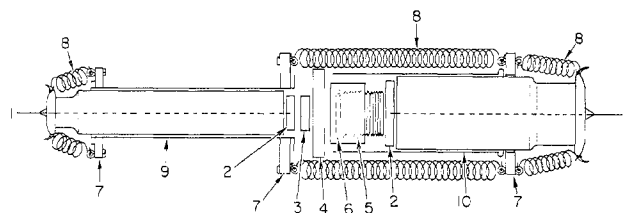
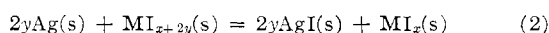


Figure 1.—The cell assembly: 1, tungsten wire leads (0.040-in. diameter); 2, graphite disk contacts; 3, silver pellet; 4, silver iodide pellet; 5, porous-faced graphite cup for iodine electrode; 6, Teflon washer; 7, brass rings; 8, springs; 9, 10-ml hypodermic syringe (0.71-in. diameter); 10, 10-ml hypodermic syringe (0.94-in. diameter).

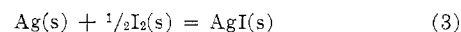
where $x = 3$ and $y = 1/2$ in the CsI₃–CsI₄ system and $x = 1 = y$ in all of the other systems investigated. The emf values were found to be a linear function of temperature for all of the cells studied over most of the temperature range of measurement. These temperature ranges together with the emf's, given in the form $E(v) = \alpha + \beta(T - 273)$, are listed in Table I.

TABLE I

$E(v) = \alpha + \beta(T - 273)$ FOR $\text{Ag} \text{AgI} \text{C}, \text{MI}_x\text{--MI}_{x+2y}$ CELLS			
Iodine source	α, v	$10^3\beta,$ $v \text{ deg}^{-1}$	Temp range, °C
I ₂ (s)	0.6830 ± 0.0009	1.50 ± 0.05	20–100
RbI–RbI ₃	0.6290 ± 0.0020	2.00 ± 0.16	55–130
NH ₄ I–NH ₄ I ₃	0.6442 ± 0.0013	1.74 ± 0.07	45–125
CsI–CsI ₃	0.6074 ± 0.0025	1.70 ± 0.16	60–150
CsI ₃ –CsI ₄	0.6551 ± 0.0011	1.75 ± 0.06	40–120

Although the potentials at temperatures below the lower limits in Table I were not reproducible, presumably owing to the iodine electrode not being poised at these low pressures, it has been assumed that the linear relations hold to 25°. At temperatures above those listed in Table I the measured emf's fell below the extrapolated linear values. This behavior may be caused in part by diffusion of iodine at these high temperatures through the cell to the silver electrode.

For cell II the reaction is



and at 25°, $E^\circ = 0.6868 \pm 0.0009 v$, $\Delta G^\circ = -15.80 \pm 0.02 \text{ kcal/mole}$, $\Delta S^\circ = 3.45 \pm 0.12 \text{ cal/mole deg}$, and $\Delta H^\circ = -14.77 \pm 0.04 \text{ kcal/mole}$. These values are in good agreement with the listed values⁵ of -15.85 kcal , 3.2 cal/mole deg , and -14.91 kcal and indicate that the cells were functioning well.

The standard free energies ΔG° for reaction 1 can be calculated from the relation

$$\Delta G^\circ = -nF(E^\circ - E) \quad (4)$$

where E and E° are the emf's of cells I and II, respectively, and $n = 2$ for all of the polyiodide systems except CsI₃–CsI₄ where $n = 1$. Expressions for $(E - E^\circ)$ and ΔG° as functions of temperature for the

(5) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

TABLE II
VALUES OF $(E - E^\circ)$, ΔG° , AND A AS FUNCTIONS OF TEMPERATURE FOR POLYIODIDE SYSTEMS

System	$(E - E^\circ), v$	$\Delta G^\circ, \text{kcal}$	A
RbI-RbI ₃	$-0.0540 + 0.000050(T - 273)$	$-2.48 + 0.00230(T - 273)$	$4053 - 0.50(T - 273)$
NH ₄ I-NH ₄ I ₃	$-0.0388 + 0.000024(T - 273)$	$-1.78 + 0.00110(T - 273)$	$3901 - 0.24(T - 273)$
CsI-CsI ₃	$-0.756 + 0.000020(T - 273)$	$-3.48 + 0.00092(T - 273)$	$4269 - 0.20(T - 273)$
CsI ₃ -CsI ₄	$-0.0279 + 0.000025(T - 273)$	$-0.65 + 0.00057(T - 273)$	$3792 - 0.25(T - 273)$

range 25–113.5° (melting point of iodine) are given in Table II.

From the free energy relations in Table II the quantities ΔG° , ΔS° , and ΔH° for reaction 1 at 25° can be calculated and are listed in Table III. Also shown in Table III in parentheses are the values of ΔG° , ΔS° , and ΔH° calculated from the solubility data of Foote, *et al.*,¹⁻³ in benzene and toluene. It has been assumed that these iodine solutions obey Henry's law. The agreement in ΔG° is very good but it is not good in ΔS° or ΔH° and the differences between the ΔH° values appear to be nonrandom. It should be pointed out that the ΔH° values stated by the above authors^{1,3} for RbI-RbI₃, CsI-CsI₃, and CsI₃-CsI₄ of -17.2, -17.5, and -15.8 kcal/mole, respectively, are for the gaseous iodine standard state, and to relate these to the data in Table III one must, of course, use the heat of sublimation of iodine at 25°, 14.88 kcal/mole.⁶

TABLE III
VALUES OF ΔG° , ΔS° , AND ΔH° AT 25° FOR THE REACTION
 $MI_x(s) + yI_2(s) = MI_{x+2y}(s)$

MI_x-MI_{x+2y}	$-\Delta G^\circ, \text{kcal}$	$-\Delta S^\circ, \text{cal/deg}$	$-\Delta H^\circ, \text{kcal}$
RbI-RbI ₃	$2.4 \pm 0.1 (2.2)^a$	$2.3 (0.3)^a$	$3.1 (2.3)^a$
NH ₄ I-NH ₄ I ₃	$1.8 \pm 0.1 (1.8)$	$1.1 (-2.3)$	$2.1 (1.1)$
CsI-CsI ₃	$3.5 \pm 0.1 (3.4)$	$0.9 (-2.7)$	$3.7 (2.6)$
CsI ₃ -CsI ₄	$0.63 \pm 0.03 (0.55)$	$0.6 (1.2)$	$0.80 (0.9)$

^a The values in parentheses are calculated from the data of Foote, *et al.*¹⁻³

The standard free energies and enthalpies of formation from the solid elements, *i.e.*, for the reaction $M(s) + (x/2)I_2(s) = MI_x(s)$, as well as the standard entropies for the solid polyiodides at 25°, have also been calculated from compiled data^{5,7} and those in Table III and are presented in Table IV.

TABLE IV
VALUES OF ΔG_f° , ΔH_f° , AND S° AT 25° FOR POLYIODIDES

Polyiodide	$-\Delta G_f^\circ, \text{kcal/mole}$	$-\Delta H_f^\circ, \text{kcal/mole}$	S°, eu
RbI ₃	80.2	81.6	53.6
NH ₄ I ₃	28.7	50.2	55
CsI ₃	83.2	84.2	58
CsI ₄	83.8	85.1	71

The iodine pressures over the polyiodide systems can be obtained by subtracting the free energy of sublimation of iodine, *i.e.*, ΔG° for $I_2(s) = I_2(g)$, from eq 4

(6) L. J. Gillespie and L. H. D. Fraser, *J. Am. Chem. Soc.*, **58**, 2260 (1936).

(7) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., 1965, Part I.

and by the use of the relation $\Delta G^\circ = -RT \ln K$. Thus for reaction 1 with $I_2(g)$ replacing $I_2(s)$ there results

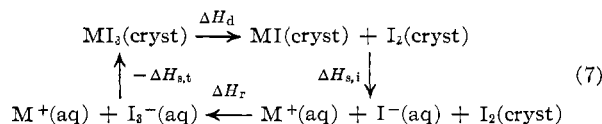
$$\ln p = (2F/RT)(E - E^\circ) + \ln p^0 \quad (5)$$

where p is the partial pressure of iodine in equilibrium with the simple iodide and triiodide (or triiodide and tetraiodide) and p^0 is the vapor pressure of solid iodine. Employing the vapor pressure expression⁸ for iodine and combining terms, we have the dissociation pressures for the polyiodide systems from 25 to 113.5° given by

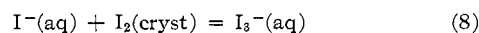
$$\log p(\text{torr}) = \frac{-A}{T} - 2.013 \log T + 16.2548 \quad (6)$$

where A is included in Table II.

Finally, with the aid of the following Born-Haber cycle the heats of solution $\Delta H_{s,t}$ of the triiodides in water can be calculated



In (7) ΔH_d represents the heat of dissociation of the solid triiodide, $\Delta H_{s,i}$ the heat of solution of the simple iodide, and ΔH_r the heat of reaction of



thus

$$\Delta H_{s,t} = \Delta H_d + \Delta H_{s,i} + \Delta H_r \quad (9)$$

where the heat of reaction 8 is taken as 0.9 kcal/mole⁷ at 25°, $\Delta H_{s,i}$ is found in standard tables,^{5,7} and ΔH_d is listed in Table III. The heats of solution for RbI₃, NH₄I₃, and CsI₃ calculated in this way are 10.3, 6.3, and 12.5 kcal/mole, respectively.

Discussion

For temperatures above 100° the iodine pressures, derived from eq 6, for solid RbI₃ and RbI mixtures are slightly lower than the measured values reported by Stepin, *et al.*⁴ For example, at 100° eq 6 yields a pressure of 2.2 torr as compared to the value 2.7 torr from the data of Stepin. However, for the temperature range 100–190°, their heat of dissociation, 16.5 kcal/mole for the gaseous iodine standard state, results in a value of 1.6 kcal/mole based on the solid. The latter value is lower than both the 3.1 kcal/mole found in the present study at 25° or Foote's value³ of 2.3 kcal/mole. Moreover, Stepin gives a sensitivity of only 1–2 torr for his measurements and the incongruent melting point⁴ 194°, found from the intersection

(8) H. T. Gerry and L. J. Gillespie, *Phys. Rev.*, **40**, 260 (1932).

of the log (vapor pressure) *vs.* $1/T$ plots for solid and liquid RbI_3 , is higher than a recently measured value⁹ of 189° . Finally, the data for solid iodine also measured by Stepin, *et al.*,⁴ yield a low heat of sublimation of 14.08 kcal/mole, compared to the accepted value of 14.88 kcal,⁵ and high values for the iodine vapor pressure, *e.g.*, at 100° 56 torr⁴ *vs.* 46 torr⁸ and at 50° 3.0 torr⁴ *vs.* 2.1 torr.⁶ The percentage differences in the iodine data are about the same as with RbI_3 , and Stepin's values differ in both systems in the same direction indicating a systematic error.

With regard to the thermodynamic data found from the measurements of Foote, *et al.*,¹⁻³ these were based on solubility determinations at only two temperatures, 6 and 25° , and required the assumption of Henry's law. The agreement in the free energy values in Table III indicates that the errors involved in the latter assumption are negligible at 25° . At 6° Foote's ΔG° values are -2.2 , -1.7 , -3.3 , and -0.54 kcal for RbI_3 , NH_4I_3 , CsI_3 , and CsI_4 , respectively, as compared to -2.5 , -1.8 , -3.5 , and -0.64 kcal found in the present study. It should be noted that the sources of error are larger in both Foote's and the present study in systems of low iodine activity and in cases where the temperature decreases. In the solubility work, analyses must be performed on small concentrations and the length of time required for equilibrium may be quite long. With the electrochemical cells the latter condition also holds and measurements must be carried out at higher temperatures to ensure a poised iodine electrode. Thus the measured range of linear potential *vs.* temperature behavior is smaller and extrapolation to 25° must be made over a longer temperature interval. However, in spite of this extrapolation, one would expect the emf values to be more accurate than either the solubility or vapor pressure measurements.

The thermodynamic data show that the affinity of the iodide salts for iodine increases with the size of the cation and decreases with temperature and additional iodine atoms. These results are influenced by a number of factors such as the differences in lattice energies and polarization effects of the pairs of salts involved in reaction 1. However, a plausibility argument concerning only the polarization effects and the triiodides can be given. Since the iodide ion-iodine bond probably results from polarization of the large iodine molecule by the negatively charged ion with the extra 5p electron becoming delocalized over the whole polyiodide entity, the cation neighbor would certainly be

(9) F. E. Rosztoczy and D. Cubicciotti, *J. Phys. Chem.*, **69**, 1687 (1965).

expected to affect the stability. Cations of high charge density (or smaller radius since only univalent ions are considered here) would polarize the polyiodide ion to a greater extent, increasing the negative charge localization near the cation, and thus decrease the stability of the species. Undoubtedly, this is an overly simplified view but appears to hold as a first approximation. Thus no stable unsolvated solid polyiodides of lithium, sodium, or potassium are known. Unfortunately, sufficient data are not yet available to indicate whether a quantitative correlation exists between the stability of the polyiodides and the size of the cation. However, a comparison of ΔG° or ΔH° for reaction 1 *vs.* $1/r_+$ (where r_+ is taken¹⁰ as 0.97, 1.33, 1.43, 1.48, and 1.68 Å for Na^+ , K^+ , NH_4^+ , Rb^+ , and Cs^+ , respectively) does suggest that ΔG° and ΔH° for the potassium system are close to zero (but ΔG° is expected to be positive since KI_3 has not been found) and for Na^+ they are definitely positive. Although solid KI_3 has not been isolated to date, $\text{KI}_3 \cdot \text{H}_2\text{O}$ does exist¹¹ at 25° , but no solvates of sodium or lithium have been found¹¹ at this temperature. This indicates that the potassium cation lies between lithium and sodium, on one hand, and ammonium, rubidium, and cesium, on the other. Indeed the ΔG° for the potassium system may be close to zero and its triiodide may exist at temperatures below 25° . However, it is impossible to predict the upper temperature of stability since the temperature dependence of ΔG° is very small in these systems and, on the basis of the other triiodides, a drop of 100° is expected to increase the stability by only about 0.1 kcal/mole.

With larger polyiodide ions as in CsI_4 (or from crystallographic data¹² Cs_2I_8 , with the I_3^- in weak interaction with an I_2 molecule), the charge on the negative species is spread over larger distances resulting in lower stabilities. The entropy values for reaction 1 are small and about equal with the possible exception of RbI_3 . It should be noted that ΔS for CsI_3 - CsI_4 is about half that in the CsI_3 and NH_4I_3 systems, and the reaction here involves only half an iodine. These data are as expected for similar reactions involving solids.

Acknowledgments.—The author thanks Mr. L. Hermo for preparing the materials and pellets and Dr. B. B. Owens for helpful discussions.

(10) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1966.

(11) N. S. Grace, *J. Phys. Chem.*, **37**, 347 (1933).

(12) E. E. Havinga, K. H. Boswijk, and E. H. Wiebenga, *Acta Cryst.*, **7**, 487 (1954).