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AEC Research and Development Report

THERMOCHEMICAL MEASUREMENTS OF PUREX PROCESS SOLUTIONS

by

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Separations Chemistry Division

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E. I. du Pont de Nemours & Co.
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ABSTRACT

Data are presented for the specific heats of representative aqueous and organic solutions of the Purex separations process. An empirical equation, accurate within four per cent of experimental values, permits the calculation of specific heats of aqueous solutions of uranyl nitrate and nitric acid throughout the ranges of process concentration. Heats of reaction are reported for the extraction of water, nitric acid, and uranyl nitrate into an organic phase composed of thirty volume per cent tributyl phosphate in kerosene.

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INTRODUCTION

Plutonium and uranium are separated and purified by a tributyl phosphate - kerosene solvent in the Purex process. The solutions of various compositions that are involved in the process have thermal properties that are not readily available. These properties were needed for evaluating heating and cooling problems, for evaluating safeguards against exceeding the flash point of the solvent, and for estimating temperatures of extraction. Heats of reaction and extraction were needed for calculation of temperatures within the contactors; these values are also expected to be useful in connection with other studies of solvent extraction.

SUMMARY

Calorimetric apparatus was assembled, and the adequacy of the equipment and technique was established by measurement of the heat capacities of several aqueous solutions containing nitric acid or uranyl nitrate. The results agreed with previous literature values within one per cent. The heat capacities of several aqueous solutions containing both uranyl nitrate and nitric acid were measured. The following equation was formulated as an expression of the data obtained at 25°C:

$$C = 1 - 0.06H - 0.39U + 0.083U^2 + 0.03HU \qquad (1)$$

where

C = specific heat of the solution, cal/gm-°C

H = molar concentration of nitric acid

U = molar concentration of uranyl nitrate

This equation was used to calculate the specific heats of aqueous uranyl nitrate - nitric acid solutions throughout the concentration range of the Purex process, with agreement within four per cent of the values obtained by direct measurement.

The heat capacity of Purex extractant, tributyl phosphate (TBP) in kerosene, was found to have a positive temperature coefficient in contradiction to earlier data in the AEC project literature. The kerosene was "Ultrasene," a special grade marketed by the Atlantic Refining Company.

The heat of extraction of water into 30 per cent TBP-"Ultrasene" is small, +0.4 kcal/mole, but values for the heats of extraction of nitric acid and uranyl nitrate are as large as -8 kcal/mole, which is sufficient to have significant effect upon the temperature profile in Purex contactors.

DISCUSSION

DESCRIPTION OF EQUIPMENT

The calorimeter (Figure 1) consisted of (1) a silvered Dewar flask enclosed in a protective container, (2) a manganin heating coil suspended within a suitably shaped glass tube filled with oil, (3) a glass stirrer driven by a small motor, and (4) a "Teflon" cover, which held in rigid alignment the heater support, the stirrer and bearing assembly, and the Beckmann thermometer.

The flask was a 750-cc, wide-mouth vacuum bottle that projected above the outer can and fitted tightly into a matching groove in the "Teflon" cover. During a run this cover was held firmly in place with bolts extending from a plate at the bottom of the flask and passing through holes in the "Teflon" cover where they were secured. The stirrer was driven by a small variable-speed motor that was coupled to the top of the shaft by a short length of heavy rubber tubing. The motor was operated independently of the remainder of the electrical equipment.

The circuit that was used to supply the energy and obtain the necessary measurements is described in Weissberger, Physical Methods of Organic Chemistry, Vol. I, Part I, page 737.(4)

SPECIFIC HEAT MEASUREMENTS

The calorimeter constant, K, was determined with water and benzene. The values of K determined by the two measurements agreed within two per cent. The specific heats of water and benzene are well established, and cover the extremes of the range for Purex solutions. A standard volume of solution was weighed into the calorimeter for each measurement and all experimental conditions were maintained as uniform as feasible from run to run. Specific heats were calculated from the relation

$$C = \frac{EIt}{4.184(\Delta T)S} - \frac{K}{S}$$

where

C = specific heat, cal/gm-°C

E = voltage across calorimeter heater

I = amperage through calorimeter heater

t = energy input time, seconds

K = calorimeter constant, cal/°C

ΔT = temperature increase due to energy input, °C

S = sample weight, grams

Aqueous Solutions

The adequacy of the apparatus was demonstrated by measurements that agreed within one per cent with previously reported values of specific heats of nitric acid solutions(1) between 0.75 and 6.0 molar. Similar evaluation with four uranyl nitrate solutions between 0.75 and 2 molar yielded results one per cent higher than values previously reported.(1) Specific heat determinations on mixed uranyl nitrate - nitric acid solutions of varying concentration of each constituent are tabulated below. Empirical Equation 1 permits calculation of the specific heats of aqueous solutions at 25°C within four per cent of the measured values. Measurements of specific heat on aqueous solutions were also made at 45 and 65°C. The accuracy at 65°C decreased to about four per cent, as shown by determinations of the calorimeter constant with diphenyl ether(2) at that temperature.

SPECIFIC HEAT, cal/gm-°C

Solutions of Uranyl Nitrate - Nitric Acid

Uranium (Molarity)	0.29	0.14	0.52	1.05	1.33	2.05
Nitric Acid (Molarity)	0.28	1.89	0.52	0.99	2.02	2.02
Measured Values, 25°C	0.87	0.83	0.81	0.67	0.61	0.53
Measured Values, 45°C	0.89	-	-	-	0.62	0.55
Measured Values, 65°C	0.91	-	-	-	0.66	0.57
Calculated from Equation 1 25°C	0.88	0.85	0.80	0.66	0.59	0.55

Tributyl Phosphate in Kerosene

Measurements of the specific heats of four extractant solutions ranging in composition from 100 per cent tributyl phosphate to 100 per cent "Ultrasene" diluent are given in the following table and are plotted in Figure 2.

SPECIFIC HEAT, cal/gm-°C

Tributyl Phosphate in "Ultrasene"

		Volume Per Cent TBP			
		0	30	60	100
Temperature, °C	25	0.48	0.47	0.45	0.43
	45	-	0.47	-	-
	65	0.53	0.51	-	0.46

These data provide an adequate basis for estimation of the specific heat of any mixture of these components. Measurements were also performed on organic solutions at 45 and 65°C, in order to determine whether a previously reported(3) negative temperature coefficient of specific heat for 30 per cent TBP in "Ultrasene" could be substantiated. The negative coefficient was not confirmed in these measurements. The positive temperature coefficient that was obtained provides assurance that the organic extractant will not demonstrate an increasing rate of temperature rise with constant heat input.

Solutions in Process Solvent

The specific heats of solutions of uranyl nitrate and nitric acid in the Purex solvent (30 per cent TBP in "Ultrasene") were calculated from data that were obtained in conjunction with determinations of the heats of extraction of these solutions. After the aqueous and organic phases had been mixed in the calorimeter and temperature equilibrium had been attained, the energy necessary to increase the temperature of the mixture 1°C was determined. The contents of the calorimeter were removed, the two phases were separated, the volume and density of each phase were measured, and the uranium and acid concentrations in each phase were determined by analyses. The specific heat of the aqueous phase was calculated from Equation 1 and the specific heat of the organic phase was then determined by difference, with an apparent accuracy of about five per cent.

At 25°C the measured specific heat of 30 per cent TBP saturated with water was 0.5 cal/gm-°C. For 30 per cent TBP solutions containing nitric acid over the concentration range 0.05 to 0.6 molar, the specific heat was calculated to be 0.55 cal/gm-°C, within 5 per cent. The specific heats at 25°C for 30 per cent TBP containing both nitric acid and uranyl nitrate are given in the following table. The specific heat values for all systems are within approximately ten per cent of that for the solute-free extractant.

SPECIFIC HEAT AT 25°C

Uranyl Nitrate and Nitric Acid in 30% TBP in "Ultrasene," Saturated With Water

$UO_2(NO_3)_2$	HNO_3	Specific Heat*
0 molar	0 molar	0.50 cal/gm-°C
0.042	0	0.49
0.34	0	0.44
0.50	0.06	0.43
0.21	0.12	0.49
0.43	0.05	0.46
0.31	0.21	0.47
0.45	0.09	0.45
0.36	0.22	0.46

* Estimated accuracy for specific heat values is ± 5 per cent.

HEAT EFFECTS IN PUREX REACTIONS

The total heat effect in Purex extraction is a combination of effects accruing from the transfer of water, nitric acid, and uranyl nitrate between phases. The individual contributions made by each component were determined by correcting for the heat produced by extraction of the other components.

The apparatus consisted of a small insulated vessel attached to the calorimeter and equipped with stirrer, heating coil, and Beckmann thermometer. The aqueous solution in the external vessel was rapidly added to the organic solution in the calorimeter after both solutions reached the same temperature. The temperature change produced by mixing the solutions was read from a Beckmann thermometer when equilibrium was reached. A measured amount of energy was added to the system and the temperature change was measured in order to determine the energy equivalent of the temperature change that was produced when the two solutions were mixed. The aqueous-organic mixture was removed from the calorimeter and the necessary analyses were performed.

The limit of accuracy of the measurement of the heat effect was three per cent as determined by measuring the heat of neutralization of 0.2 molar sodium hydroxide with 0.2 molar nitric acid ($\Delta T = 1.38°C$). Three per cent accuracy was probably not attained for heat effects producing less than 0.5°C change in temperature. Most of the extractions with water and nitric acid produced temperature changes of less than 0.5°C, and the accuracy for each individual measurement was estimated on the basis of the ΔT and was included in the tabulation. All uranium extractions except one produced temperature changes greater than one degree, so that the accuracy was not seriously affected by the ΔT. However, in this case the cumulative errors due to correction for acid extraction limited the accuracy and it was estimated that the errors were approximately five per cent for the values tabulated.

The heat effects produced by individual components of the system were studied by first measuring the effect of adding water to a dry solution of 30 per cent tributyl phosphate in "Ultrasene." Two such measurements gave an average value of +0.4 kcal per mole of water extracted. The solubility of water was small, 7.5 mg per liter in the organic phase in equilibrium with water. The heat effects were therefore so small ($\Delta T < 0.2°C$) that duplicate runs differed by 20 per cent, but the corrections made to subsequent data were based on the small heat effects and were subject only to small errors.

The heat of extraction of nitric acid into the organic solvent was determined by adding aqueous nitric acid to extractant, measuring the heat effect, and correcting the heat effect for that due to extraction of water. The data obtained are presented in the following table and in Figure 3.

HEAT OF EXTRACTION

Nitric Acid into 30 per cent TBP in "Ultrasene"

(kcal/mole HNO_3 Extracted, Corrected for H_2O Extraction)

Molarity HNO_3 (aqueous)	0.41	0.78	1.53	3.07
Molarity HNO_3 (organic)	0.06	0.15	0.34	0.71
Heat of Reaction	-3.9	-3.4	-2.7	-1.6
Estimated Accuracy, Per Cent	±25	±6	±4	±4

The heats of extraction of uranyl nitrate, from both neutral and nitric acid solution in water, were determined similarly. The observed heat effects were corrected for effects of both water and nitric acid to calculate the individual effect of extraction of the uranyl nitrate. The data are presented in the following table and in Figure 4.

HEATS OF EXTRACTION

Uranyl Nitrate into 30 per cent TBP in "Ultrasene"

Molarity HNO_3 (aqueous)	0	1.08	2.15	0	3.06	1.01	2.11
Molarity HNO_3 (organic)	0	0.12	0.21	0	0.22	0.05	0.06
Molarity $UO_2(NO_3)_2$ (aqueous)	0.053	0.047	0.045	0.36	0.06	0.36	0.90
Molarity $UO_2(NO_3)_2$ (organic)	0.042	0.21	0.31	0.33	0.36	0.43	0.50
*Heat of Extraction [kcal/mole $UO_2(NO_3)_2$ transferred to organic phase]	-1.5	-4.5	-4.7	-5.5	-5.9	-6.3	-7.7
Heat of Extraction (Smoothed values, Figure 4)	-1.2	-4.2	-5.2	-5.5	-5.9	-6.5	-7.3

* Measured, corrected for H_2O and HNO_3 extracted.

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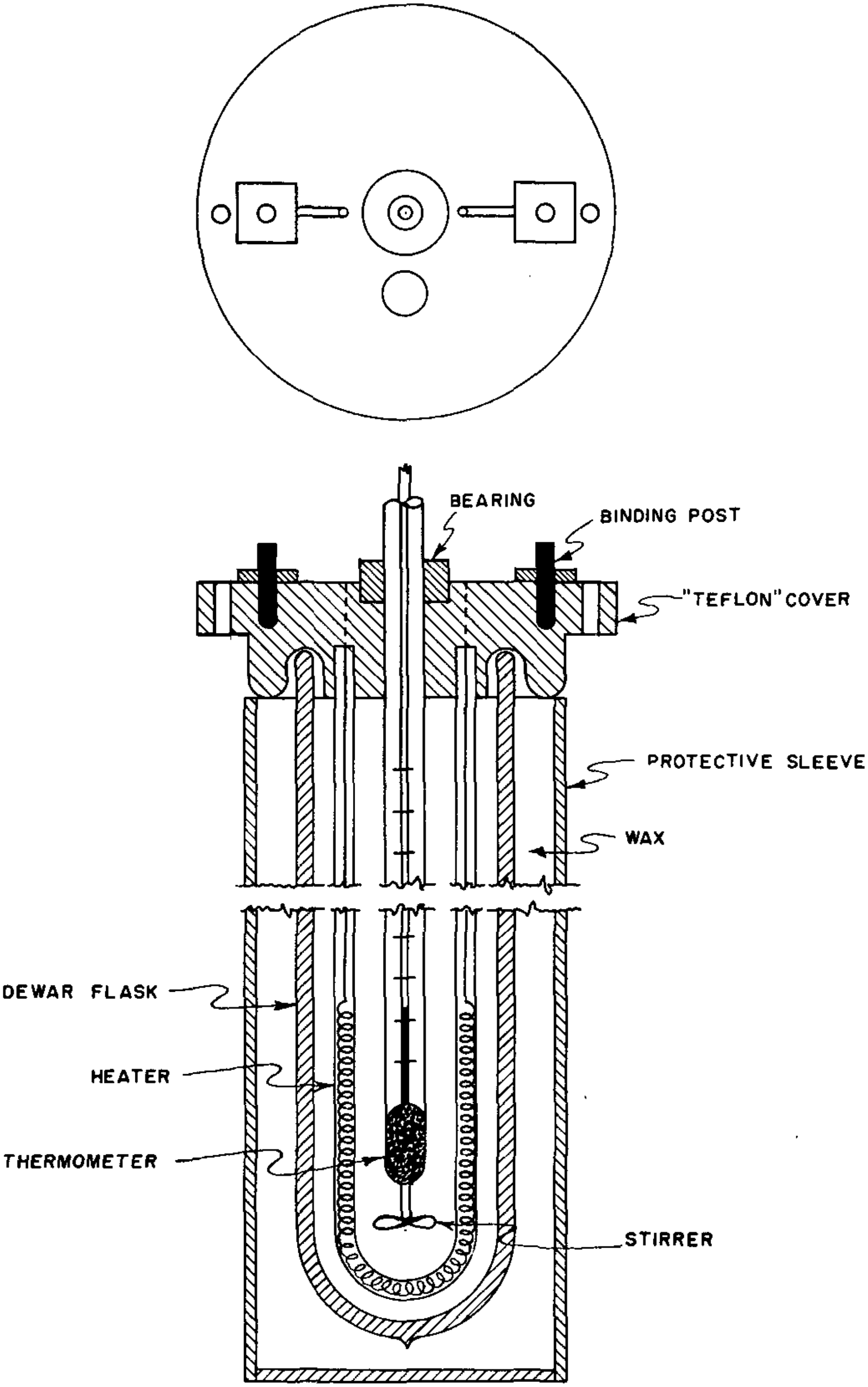
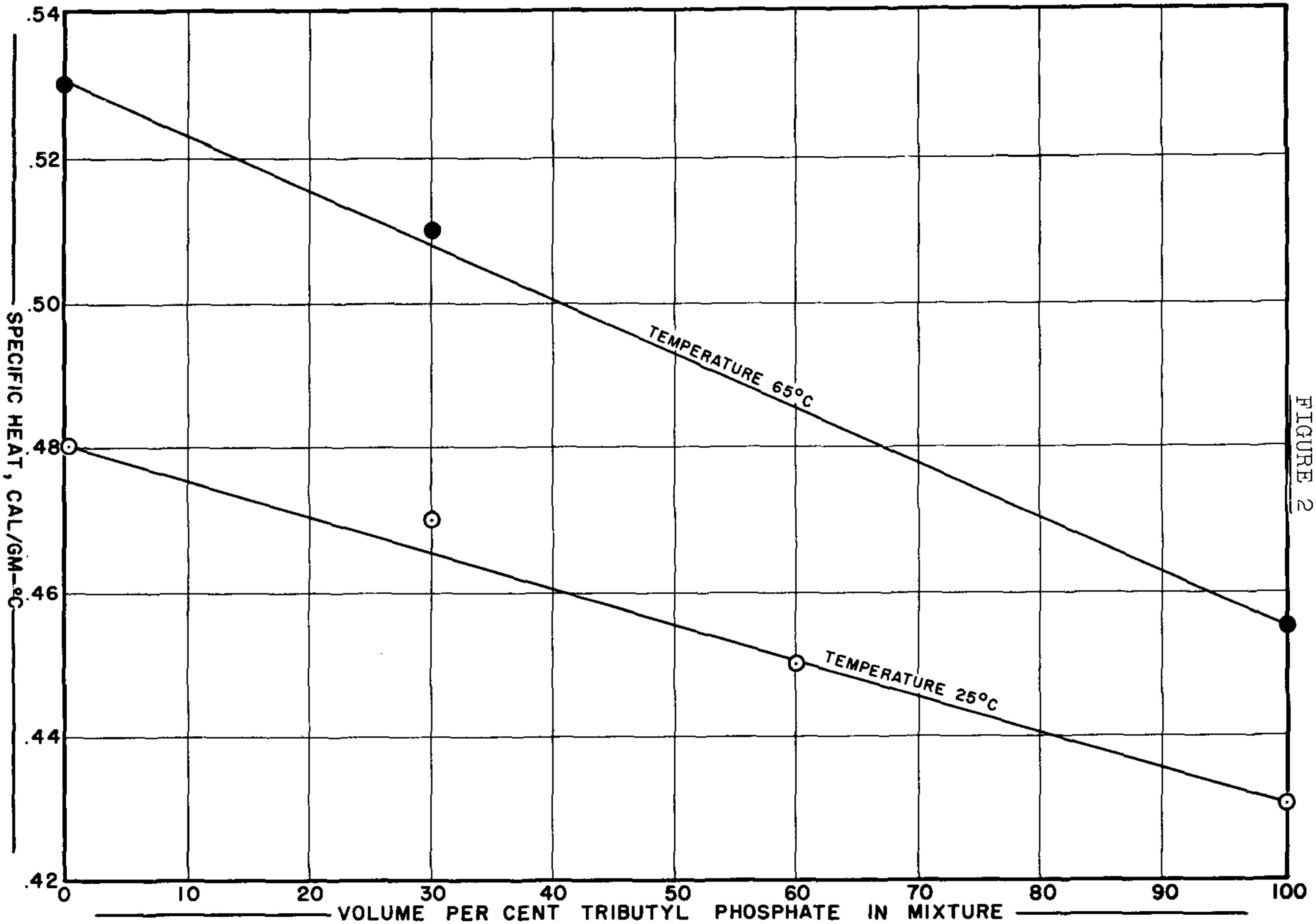
FIGURE 1

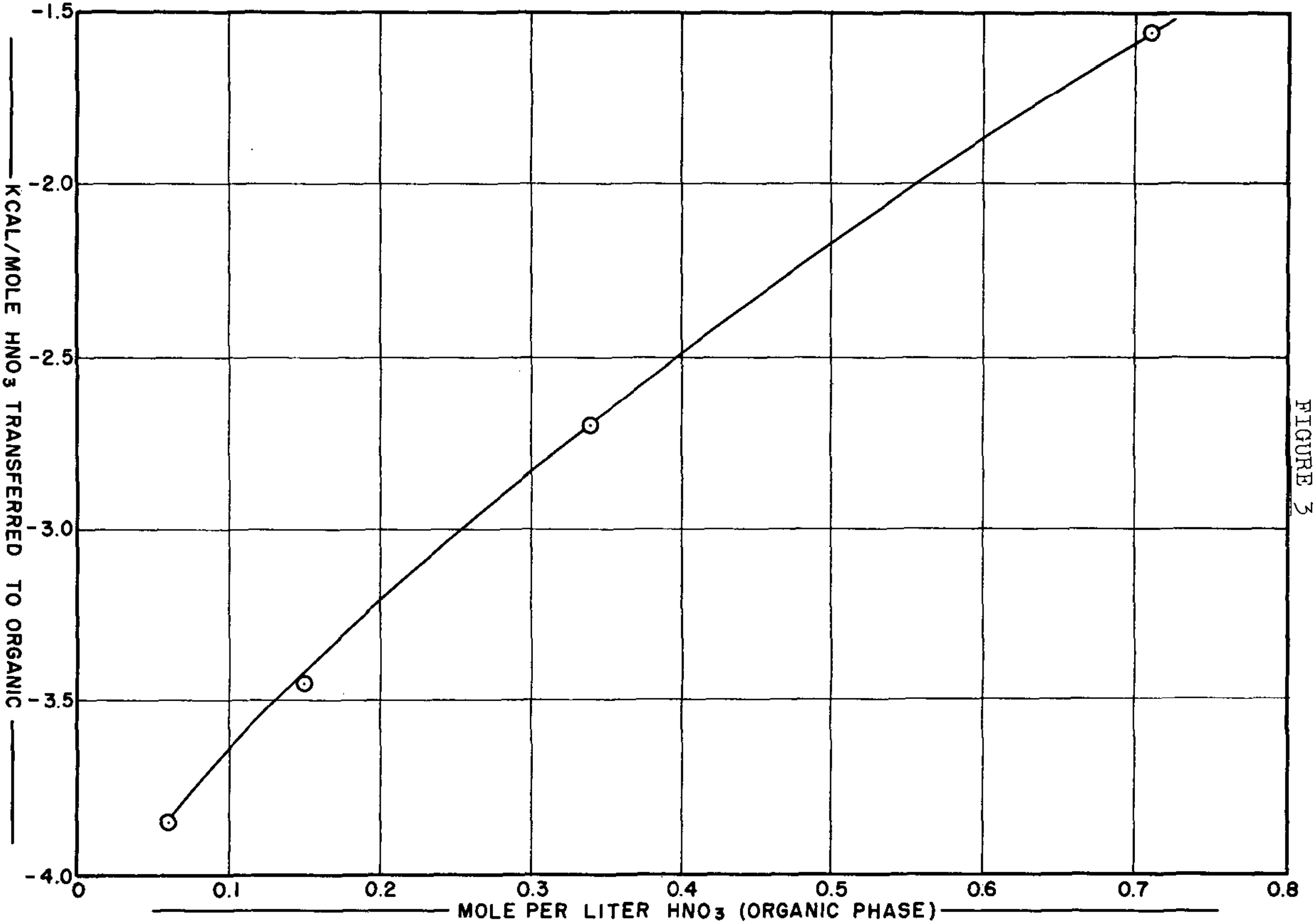


CALORIMETER

FIGURE 2



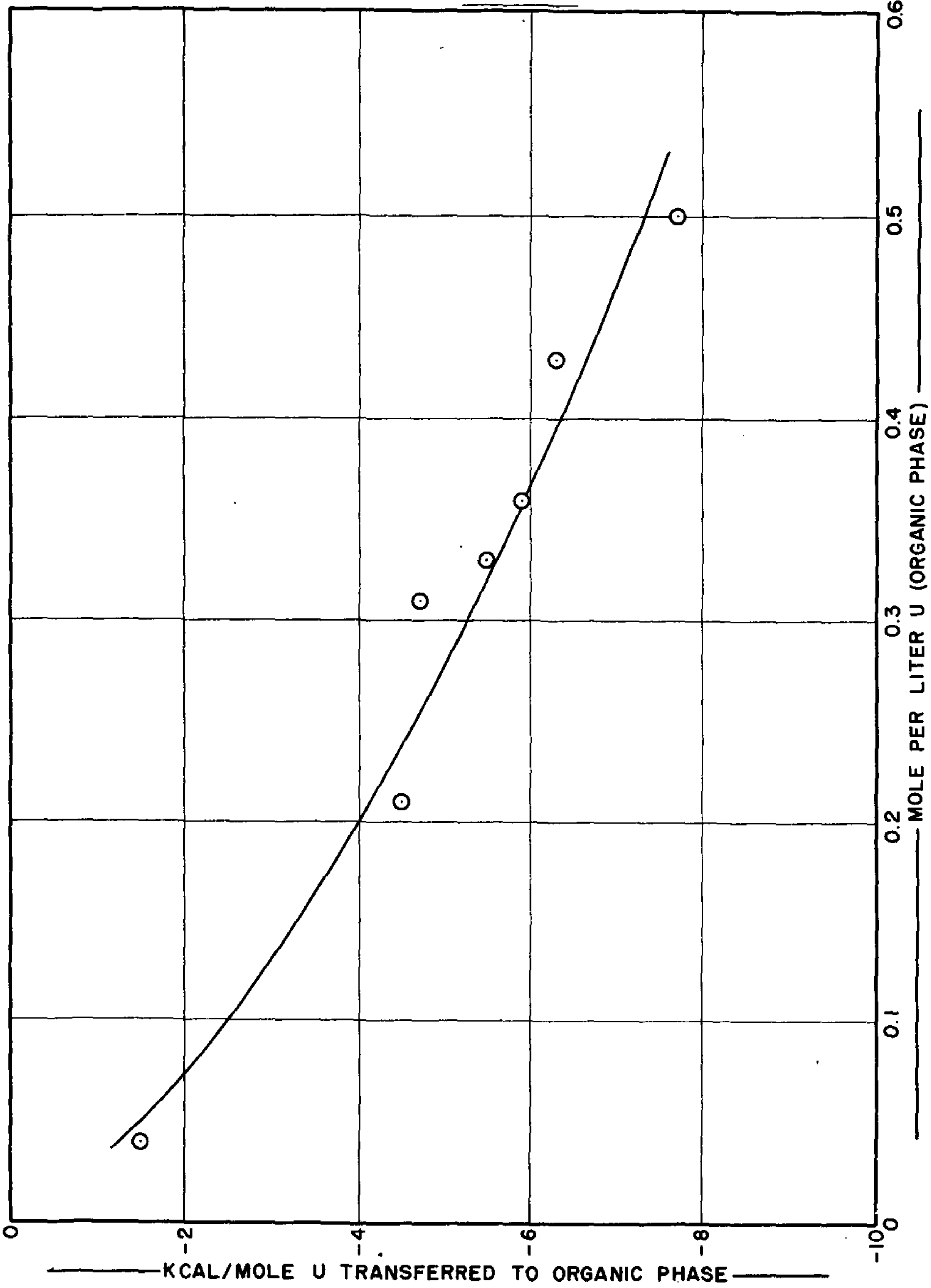
SPECIFIC HEATS OF TBP-"ULTRASENE" MIXTURES



HEAT OF EXTRACTION OF NITRIC ACID FROM AQUEOUS PHASE TO 30% TBP (IN "ULTRASENE")

FIGURE 3

FIGURE 4



HEAT OF EXTRACTION OF URANYL NITRATE FROM AQUEOUS PHASE TO 30% TBP (IN "ULTRASENE")