In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

3/17/65
b

THE SOLUBILITIES OF BENZENE AND OTHER RELATED HYDROCARBONS IN H_2O AND D_2O

A THESIS

Presented to

The Faculty of the Graduate Division

by

Chia-chi Yang

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

Georgia Institute of Technology

December, 1967

THE SOLUBILITIES OF BENZENE AND OTHER RELATED HYDROCARBONS IN H_2O AND D_2O

Approved:

Chairman

Date approved by Chairman: 12 Dec 1967

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. R. A. Pierotti for his interest, assistance, guidance, and encouragement as thesis advisor. The experimental work in this investigation could not have been carried out without the assistance of Dr. J. J. McAlpin and Mr. R. N. Ramsey. The author also wishes to thank Mr. J. M. McKelvey and Mr. J. D. Delay for their help in the computer programming. The author wishes especially to thank Mr. J. L. Carden for his help in English grammar.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (Concluded)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Concluded)

SUMMARY

Flame-ionization gas chromatography was used to determine the solubilities of some hydrocarbons in H_2O and D_2O. Their thermodynamic properties, calculated from the temperature dependence of the solubilities, were compared with each other and also compared with the results from McAuliffe, Arnold, et al., Franks, et al., etc. It was found that the solubilities in H_2O were higher than in D_2O regardless of the concentration unit (i.e., molar, molal, or mole fraction) used. For benzene and toluene, ΔH^o and ΔS^o in D_2O were higher at higher temperature than ΔH^o and ΔS^o in H_2O; at the lower temperature, the opposite behavior was observed. ΔH^o and ΔS^o exhibit the opposite behavior for ethylbenzene from that observed for benzene and toluene. For isopropylbenzene, ΔH^o and ΔS^o for D_2O solutions were lower than corresponding values for H_2O solutions at all temperatures investigated, and in D_2O ΔH^o and ΔS^o were independent of temperature over the temperature range studied here.

ΔC_P^o for benzene and toluene in H_2O were higher than in D_2O at all temperatures. For isopropylbenzene, the values of ΔC_P^o in D_2O were zero (independent of temperature), and in H_2O were negative. ΔC_P^o for ethylbenzene in H_2O was higher than in D_2O. Generally, the values of ΔC_P^o increased as temperature increased except for those of ethylbenzene in H_2O and isopropylbenzene in D_2O. In the last two systems, ΔC_P^o were independent of temperature.

CHAPTER I

INTRODUCTION

The solubilities of benzene, toluene, ethylbenzene, and isopropylbenzene in H_2O at 25°C have been determined by many investigators,[1-10] but no solubilities of these hydrocarbons in D_2O had been determined. The purpose of this investigation was to determine the solubilities of these hydrocarbons in H_2O and D_2O at different temperatures ranging from 10°C to 40°C. The thermodynamic properties which were calculated for the solutions are tabulated and compared with one another.

Solute concentrations were determined in this investigation by means of a flame-ionization gas chromatograph (Perkin-Elmer 154-D Flame-Ionization Gas Chromatograph). Two major considerations in the choice of flame ionization chromatographic analysis were as follows: (1) the high sensitivity of the flame-ionization detector (0.1 ppm of organic material per 50 µl of H_2O solution could be detected[1]), and (2) the ability of the chromatographic column to separate any impurities which have different retention times from the organic material of interest.

CHAPTER II

REAGENTS, EQUIPMENT, AND PROCEDURE

Reagents

The following reagents were used:

(1) Benzene, Fisher Scientific Company, 99 mole percent, pure and free of thiophene.

(2) n-Hexane, Fisher Scientific Company, spectrophotometric grade.

(3) Toluene, Baker Chemical Company, analyzed reagent grade.

(4) Ethylbenzene, Eastman Organic Chemicals, reagent grade.

(5) Isopropylbenzene, Eastman Organic Chemicals, reagent grade.

These reagents were used as received.

The D_2O used was obtained from the Atomic Energy Commission of the United States and bottled at the Georgia Institute of Technology. The percentage of H_2O in the D_2O had been determined by nuclear magnetic resonance at the Georgia Institute of Technology and found to be 1.1 percent by weight.

The same solubilities were obtained using either laboratory distilled water or triply distilled water; therefore, untreated laboratory distilled water was used in the study.

Equipment

Constant Temperature Water Bath and Rotating Basket

The temperature of the water bath was controlled by a YSI model

71 thermistor which controlled the temperature to within ± 0.1°C. The thermometer used was calibrated by a 8163 platinum resistance thermometer which had been calibrated by Leeds and Northrup. The heating element was a 500-w metallic bar heater immersed in the water at one end of the bath. A refrigerating unit located under the bath was used to cool the entire system. An ordinary stirrer was placed at the same end of the bath as the heater. The stirrer was found to provide sufficient circulation to eliminate appreciable temperature gradients in the bath.

The rotating basket was made from a 4" x 10" x 3" metallic test tube stand. A short piece of copper rod was welded to each end of the tube stand and the whole thing was then mounted on two pieces of aluminum plate through Teflon bearings. The complete assembly was sprayed with yellow zinc chromate primer to prevent oxidation. A 60 rpm heavy duty motor was used to rotate the basket.

Fractionator

A fractionator filled with ascarite was used to separate the water from the dissolved hydrocarbons before the vapor entered the chromatographic column. The fractionator, a modification of the one reported by McAuliffe,[1] was a 10-inch U-tube made of 10-mm glass tubing. Both ends of the U-tube were sealed to one-fourth inch Kovar seals which were connected into the chromatograph flow stream by means of one-fourth inch Cajon fittings and O-rings. The fractionator was easily removed for drying agent replacement. The fractionator was filled with 8-20 mesh ascarite held in by glass wool. It was inserted in between the injection port and the detector block. The water part of the injected sample solution was held by the ascarite in the fractionator and thus could not enter the column. The ascarite packing was replaced after exposure to about 1,000 μl of solution.

Chromatographic Column

The chromatographic column used was a one-fourth inch Perkin-Elmer Vapor Fractometer Column "R", 2 m long, coated with polypropylene glycol (UCON OIL LB-550-X). The support material was GC-22, 60-80 mesh. The column was operated at 100°C for the detection of benzene and toluene and at 150°C for the detection of ethylbenzene and isopropylbenzene. Nitrogen gas was used as the carrier gas, because, according to Hoffmann and Evans,[11] nitrogen gas offers a greater flame-ionization detector sensitivity and also gives higher peaks in the chromatogram than helium gas. The flow rate of hydrogen gas was 15 cc per minute and the flow rate of USP compressed air was 75 cc per minute. These were found to be the optimum conditions.

Procedure

One ml of hydrocarbon and 10 ml of solvent were put into a 10-ml rubber-capped bottle. The portion of the rubber cap exposed to the solution was covered with a piece of aluminum foil to keep the cap from contacting the hydrocarbons, otherwise swelling of the rubber cap was observed. The bottles were put into the rotating basket which was immersed in a constant temperature water bath. The bottles were held loosely in the lattice of the basket by rubber bands. After rotating at least five hours at 60 rotations per minute, the rotation was stopped and the bottles were set vertically with the mouths of the bottles down and allowed to remain thus for at least three hours in order to insure complete separation of the two liquid layers. The water solution was then sampled using a 10 microliter

Hamilton syringe. It was observed that some hydrocarbon adhered to the aluminum foil septum liner. In order to eliminate any of this hydrocarbon which entered the syringe needle by capillary action, the syringe plunger was retracted prior to insertion and after insertion the entrapped air was pushed through the needle thus forcing out any material in the needle. The syringe needle was wiped clean with Kimwipes before the needle was inserted into the injection port of the gas chromatograph. When a sample of another hydrocarbon was being taken, both the syringe plunger and the syringe needle were wiped with Kimwipes.

The same solutions, septum bottles, and caps were used run after run. A run is defined here as a determination of the solubilities of the various hydrocarbons in D_2O and H_2O at a given temperature. Before reusing the rubber caps, they were boiled in dilute "Alconox" solution for about two hours, then rinsed and boiled in tap water for another two to three hours. They were finally rinsed with distilled water and dried with Kimwipes.

Since some hydrocarbon was absorbed by the caps, after the solutions were used for a run, a small amount of hydrocarbon was added to insure that the fresh cap, inserted prior to next run, would not absorb all the hydrocarbon present. The solution was replaced if the hydrocarbon layer became cloudy or colored.

The peak areas of the chromatogram were measured by using a planimeter. The concentration of the hydrocarbons in H_2O or D_2O solutions were determined by comparing the measured area with a calibration curve. The calibration curve was made by plotting the peak areas obtained against the amount of hydrocarbon injected. Since the peak areas of the chromatogram are directly proportional to the amount of hydrocarbon injected only when the concentration of hydrocarbon is very low, dilute solutions of each of these four hydrocarbon solutions were used. These concentrations ranged from less than 0.1 percent for isopropylbenzene to about one percent for benzene. In preparing the dilute solutions, n-hexane was used as the solvent for toluene, ethylbenzene, and isopropylbenzene; toluene was used as the solvent for benzene. Since a large amount of solvent was present, it took an appreciable time for the solvent to be eluted. When a solute peak appeared before the solvent was completely eluted, a French curve was used to determine the boundary of the solute peak.

CHAPTER III

COMPUTATIONS AND RESULTS

The solubilities of the four hydrocarbons studied in this work were determined at different temperatures and are listed in Table 1 and Table 2 in terms of mole fractions. The results were obtained by comparing the chromatogram peak areas for each sample with the calibration curve for the appropriate hydrocarbon and then converting to the equivalent number of microliters of calibration solution. From the density and concentration of the calibration solution, the amount of hydrocarbon dissolved was found. Since the concentration of the solution was very low, the density of the calibration solution was considered to be the same as that of the pure solvent within experimental error. (The concentration of n-hexane-benzene solution was the highest among the four calibrating solutions; the density of this solution calculated from the molar volumes of n-hexane and benzene was found to be less than one percent higher than that of pure n-hexane.) The density of 98.9 weight percent or 98.8 mole percent D_2O at various temperatures was computed with the following formula given by Kirshenbaum[12] using the density data of Steckel and Szapiro[13] for both 100 percent D_2O and 100 percent H_2O and assuming an additive molar volume relationship

$$d = \frac{N_1 M_1 + N_2 M_2}{N_1 \frac{M_1}{d_1} + N_2 \frac{M_2}{d_2}} \qquad (1)$$

Table 1. Solubility of Hydrocarbons in H_2O

Hydrocarbon	Temperature °C	X_2/P_2 (Mole Fraction/Atm.) This Work	Other Work
Benzene	10	0.00532 ± 0.00015	
	15	0.00428 ± 0.00010	
	20	0.00346 ± 0.00012	
	25	0.00310 ± 0.00015	0.00327[1]
			0.00314[2]
			0.00316[3]
			0.00317[4]
			0.00317[5]
			0.00329[6]
			0.00326[7]
			0.00267[8]
	30	0.00234 ± 0.00013	
	35	0.00200 ± 0.00006	
	40	0.00179 ± 0.00014	
Toluene	10	0.00710 ± 0.00029	
	15	0.00520 ± 0.00024	
	20	0.00396 ± 0.00018	
	25	0.00314 ± 0.00014	0.00268[1]
			0.00279[2]
			0.00276[5]
			0.00327[6]
	30	0.00259 ± 0.0001	0.00245[9]
	35	0.00203 ± 0.00012	
	40	0.00172 ± 0.0001	
Ethylbenzene	10	0.00566 ± 0.00046	
	15	0.00385 ± 0.00016	
	20	0.00273 ± 0.00017	
	25	0.00203 ± 0.0006	0.00207[1]
			0.00225[2]
			0.00284[6]
			0.00192[9]
	30	0.00175 ± 0.00010	0.00229[10]
	35	0.00153 ± 0.00009	
	40	0.00139 ± 0.00013	

Table 1. Solubility of Hydrocarbons in H_2O (Concluded)

Hydrocarbon	Temperature °C	X_2/P_2 (Mole Fraction/Atm.) This Work	Other Work
Isopropylbenzene	10	0.00507 ± 0.00021	
	15	0.00397 ± 0.00037	
	20	0.00309 ± 0.00018	
	25	0.00243 ± 0.00016	0.00169[1] 0.00246[10]
	35	0.00140 ± 0.00013	
	40	0.00084 ± 0.00008	

Table 2. Solubility of Hydrocarbons in D_2O

Hydrocarbon	Temperature °C	X_2/P_2 (Mole Fraction/Atm.) This Work
Benzene	10	0.00493 ± 0.00048
	15	0.00406 ± 0.00018
	20	0.00304 ± 0.00015
	25	0.00257 ± 0.00011
	30	0.00206 ± 0.00010
	35	0.00179 ± 0.00006
	40	0.00160 ± 0.00005
Toluene	10	0.00614 ± 0.00035
	15	0.00446 ± 0.00026
	20	0.00344 ± 0.00011
	25	0.00278 ± 0.00023
	30	0.00231 ± 0.00015
	35	0.00183 ± 0.00005
	40	0.00152 ± 0.00007
Ethylbenzene	10	0.00465 ± 0.00025
	15	0.00345 + 0.00027
	20	0.00267 ± 0.00013
	25	0.00188 ± 0.00013
	30	0.00165 ± 0.00016
	35	0.00143 ± 0.00006
	40	0.00127 ± 0.00006
Isopropylbenzene	10	0.00433 ± 0.00042
	15	0.00379 ± 0.00011
	20	0.00300 ± 0.00016
	30	0.00218 ± 0.00006

where

M_1 = molecular weight of protium oxide

M_2 = molecular weight of deuterium oxide

N_1 = mole fraction of protium oxide

N_2 = mole fraction of deuterium oxide

d = density of the mixture

d_1 = density of protium oxide

d_2 = density of deuterium oxide

The densities of 98.8 mole percent D_2O calculated at different temperatures are listed in Table 3.

Table 3. Density of 98.8 Mole Percent D_2O

Temperature, °K	Density, g/ml
283.05	1.10474
288.15	1.10472
293.10	1.10418
298.28	1.10328
303.23	1.10207
308.14	1.10055
313.08	1.09877

The solubility data in H_2O determined in this investigation for benzene at room temperature agreed with those results reported by Morrison and Billett,[2] Franks, Gent, and Johnson,[3] Arnold, Plank, Erickson, and

Pike,[4] and Andrews and Keefer,[5] but was somewhat lower than those from McAuliffe,[1] Bohon and Claussen,[6] and McDevit and Long.[7] It was much higher than Durand's[8] result. The solubility of toluene in H_2O was higher than those of McAuliffe, Andrews, and Keefer, and Morrison and Billett, but was lower than the value from Bohon and Claussen. The result obtained for ethylbenzene was almost the same as that of McAuliffe, and lower than those of Andrews and Keefer, Morrison and Billett, and Bohon and Claussen, but was much higher than that of Fuhner.[9] The solubility of isopropylbenzene agreed very well with that of Andrews and Keefer[10] but was higher than McAuliffe's.

The variations of the logarithm of the solubility of the hydrocarbons in H_2O and D_2O as a function of the reciprocal of the absolute temperature were plotted and were compared in Figures 1-4 for benzene, toluene, ethylbenzene, and isopropylbenzene, respectively. All the results in this investigation were calculated for a standard state of 760 Torr vapor pressure. The vapor pressures of the hydrocarbons at different temperatures were calculated from the following equation[14]

$$\log_{10}P = A - \frac{B}{C + t} \qquad (2)$$

where

P = pressure in Torr

t = degree in Centigrade

A, B, and C = constants

The values of the constants, A, B, and C, for each of the hydrocarbons used in this work are listed in Table 4.

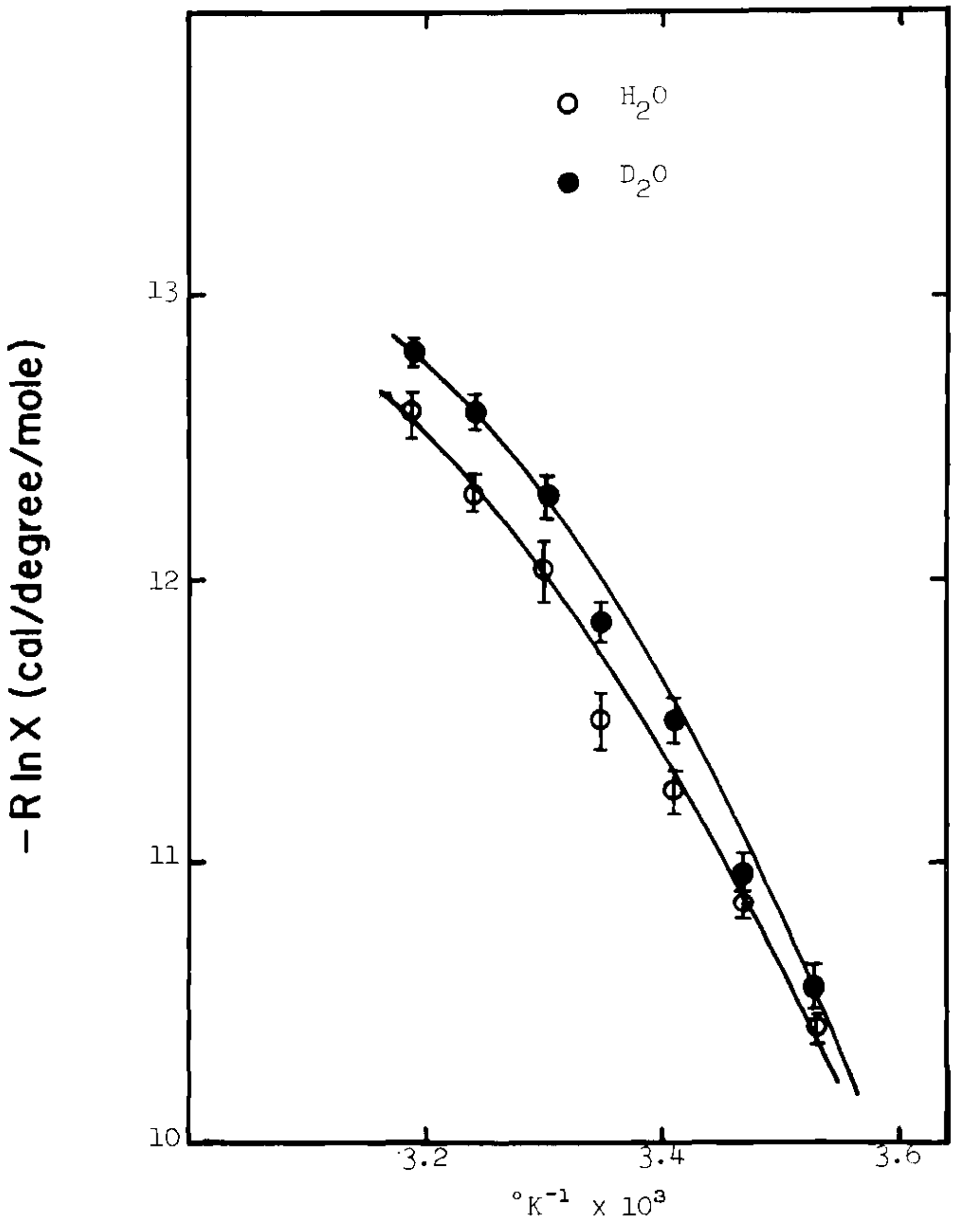

Figure 1. Solubility of Benzene in H_2O and D_2O as a Function of Temperature

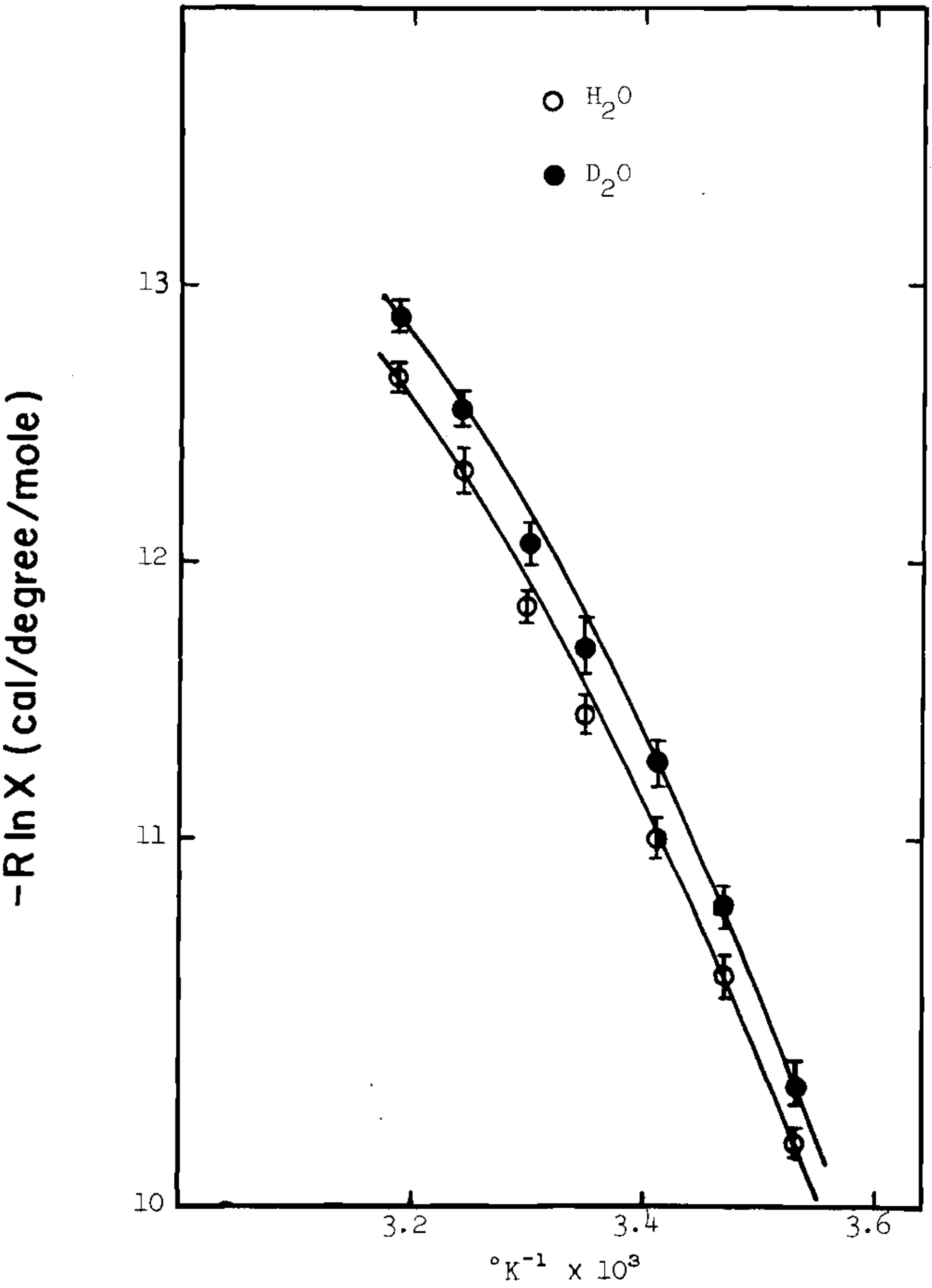

Figure 2. Solubility of Toluene in H_2O and D_2O as a Function of Temperature

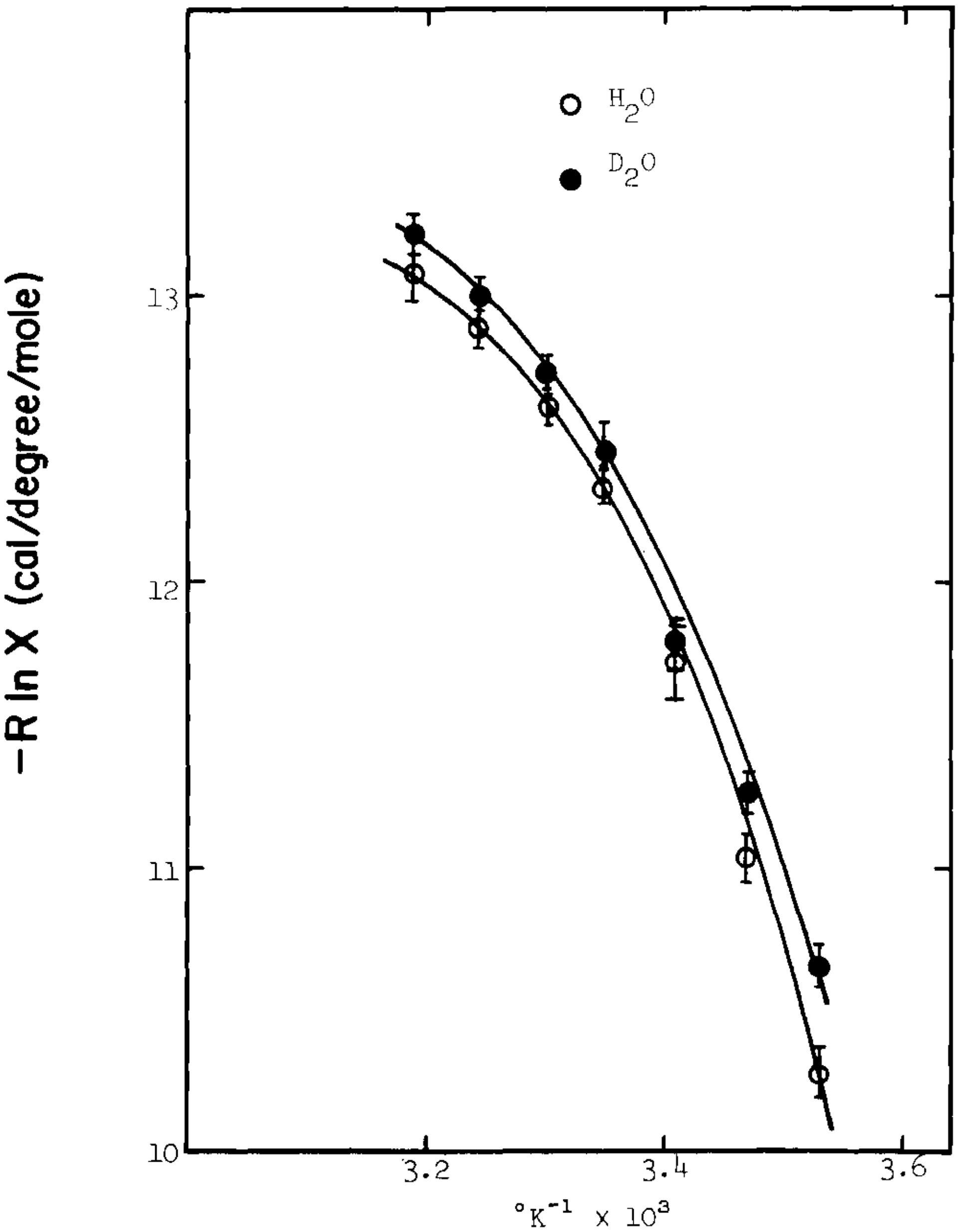

Figure 3. Solubility of Ethylbenzene in H_2O and D_2O as a Function of Temperature

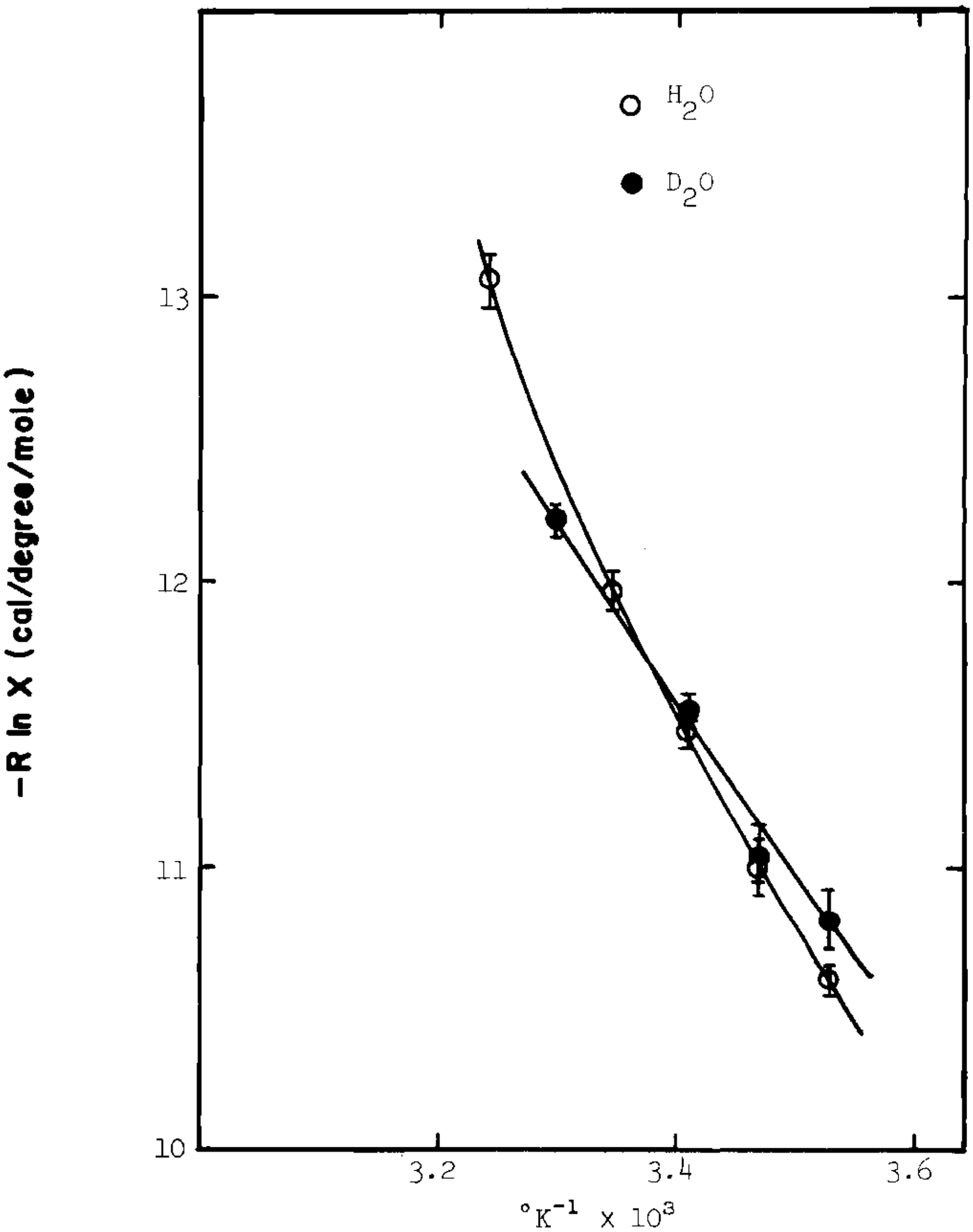

Figure 4. Solubility of Isopropylbenzene in H_2O and D_2O as a Function of Temperature

Table 4. Values for Constants A, B, and C

	Benzene	Toluene	Ethylbenzene	Isopropylbenzene
A	6.90565	6.95464	6.95719	6.95142
B	1211.033	1344.800	1424.255	1491.297
C	220.790	219.482	213.206	207.140

The solubilities of the hydrocarbons were always higher in H_2O than in D_2O, no matter whether they were molar or molal concentrations. These results were different from the results obtained by Kresheck, Schneider, and Scheraga[15] for propane and butane. They found that, on a mole fraction or molar basis, the solubilities in D_2O were higher than that in H_2O, but on a molal basis, the solubilities in D_2O were lower. The difference between the solubilities of hydrocarbons in H_2O and D_2O in this investigation decreased only slightly as the temperature increased. However, the solubilities of butane and propane in H_2O and D_2O were almost the same at 45-55° C, as reported by Kresheck, et al.

Since the standard free energy change is dependent upon the standard state chosen (concentration units), it was decided to use a mole fraction basis for the standard state of the solution and a one atm. standard state for the gas phase. The thermodynamic properties reported below therefore correspond to the process

$$A\ (g,\ 1\ atm) \rightarrow A\ (solution,\ X) \qquad (3)$$

The relation between the standard free energy of solution and the mole fraction of solute for the above process is

$$\Delta G^{o} = -RT\ln X_2/P_2 = RT\ln K_H \tag{4}$$

where

ΔG^{o} = standard Gibbs free energy change

X_2 = mole fraction of solute

P_2 = partial pressure of solute in atmospheres

K_H = Henry law constant

R and T have their usual meanings

Since the variation of ΔG^{o} with temperature has been determined in this investigation, the enthalpy of the above process can be determined. The values of standard enthalpy change for the hydrocarbons at different temperatures were found using the equation

$$\left(\frac{\partial \frac{\Delta G^{o}}{T}}{\partial \frac{1}{T}}\right)_P = \Delta H^{o} \tag{5}$$

From the slopes of the $\Delta G^{o}/T$ versus $1/T$ curves, which are shown in Figures 1-4, the values of ΔH^{o} for benzene, toluene, ethylbenzene, and isopropylbenzene in H_2O and D_2O were obtained and are shown in Figures 5-8.

The slope of ΔH^{o} versus T yields ΔC_P^{o}, i.e.

$$\Delta C_P^{o} = \left(\frac{\partial \Delta H^{o}}{\partial T}\right)_P \tag{6}$$

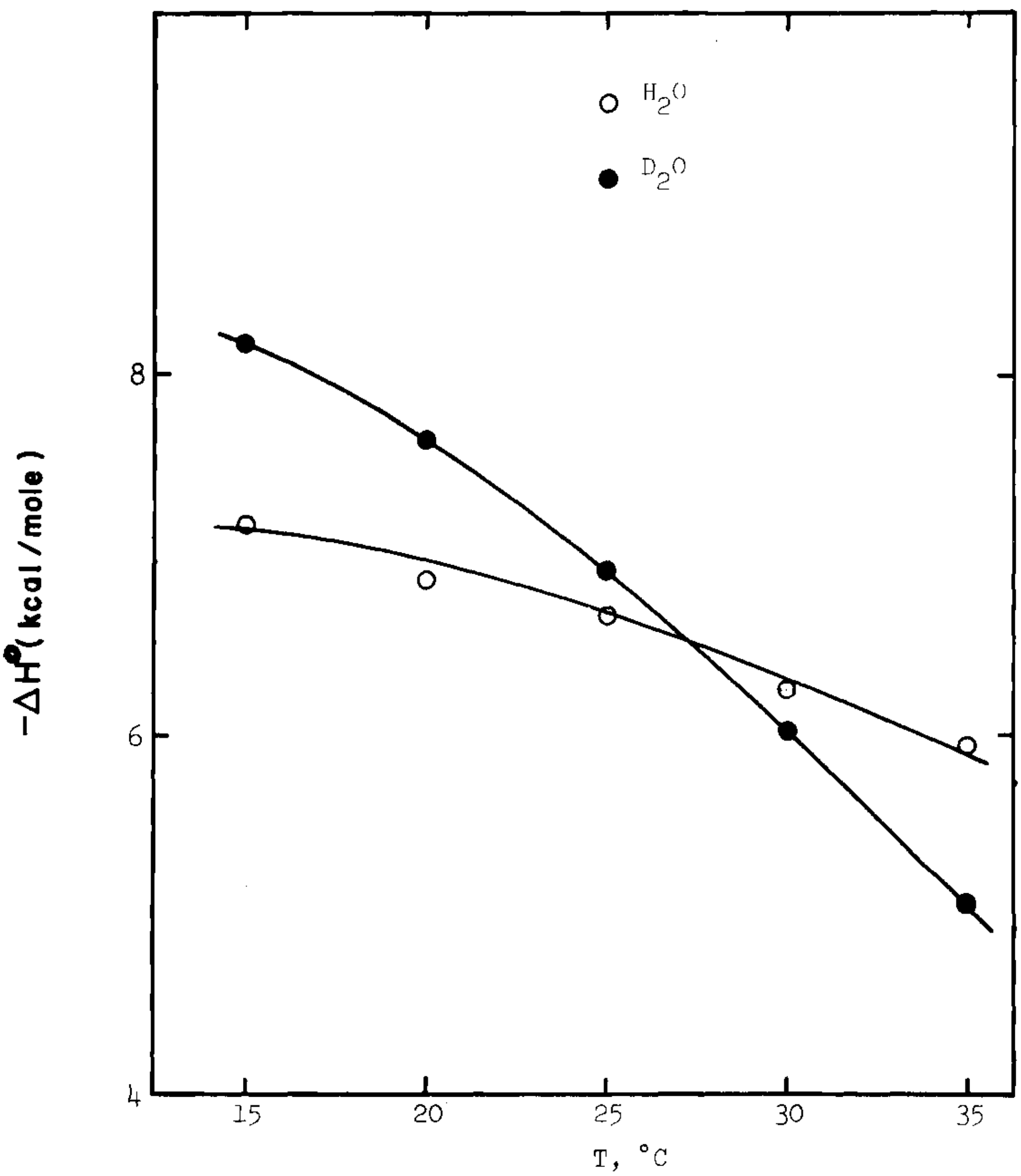

Figure 5. $-\Delta H^{o}$ of Benzene in H_2O and D_2O as a Function of Temperature

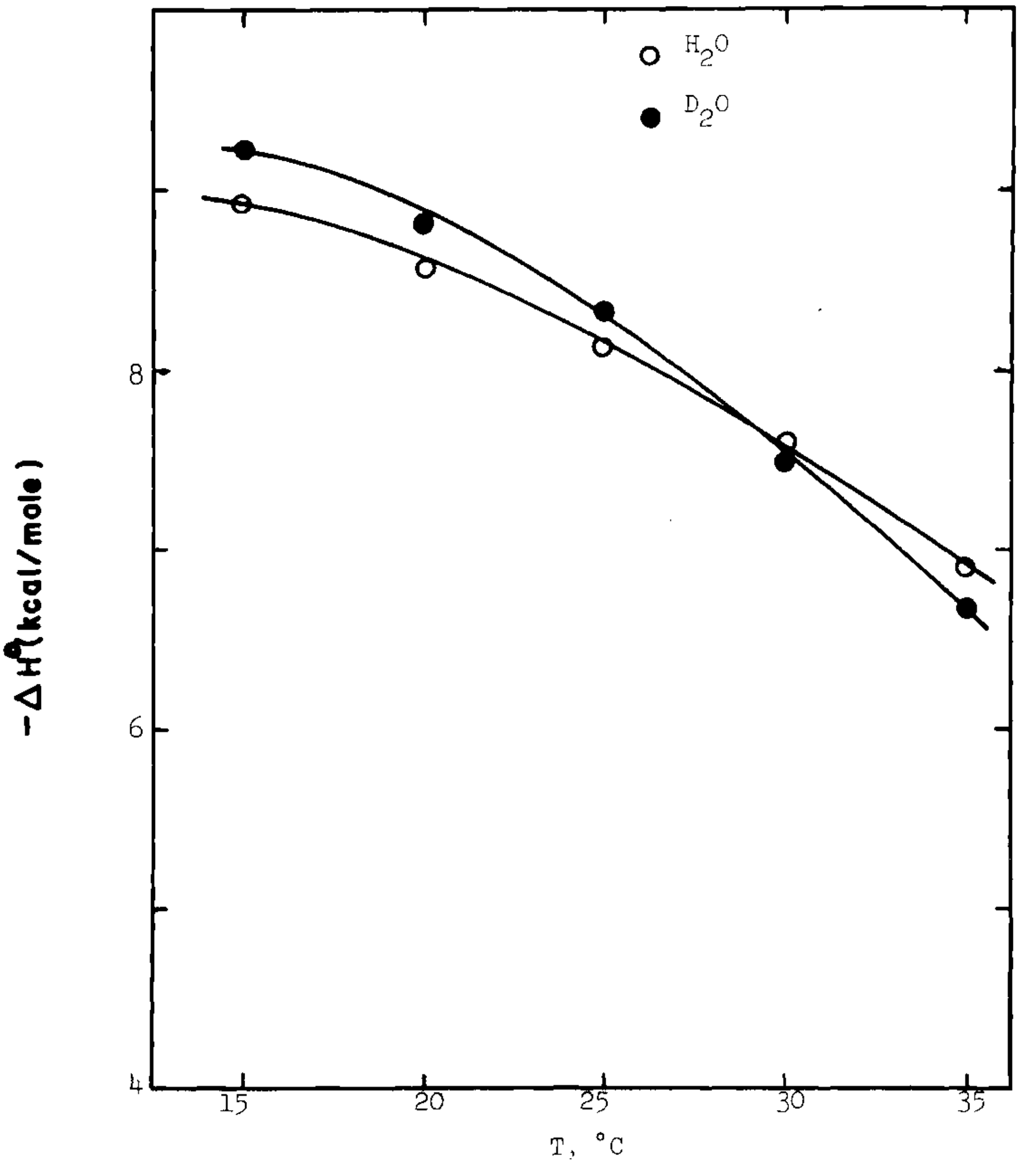

Figure 6. $-\Delta H^o$ of Toluene in H_2O and D_2O as a Function of Temperature

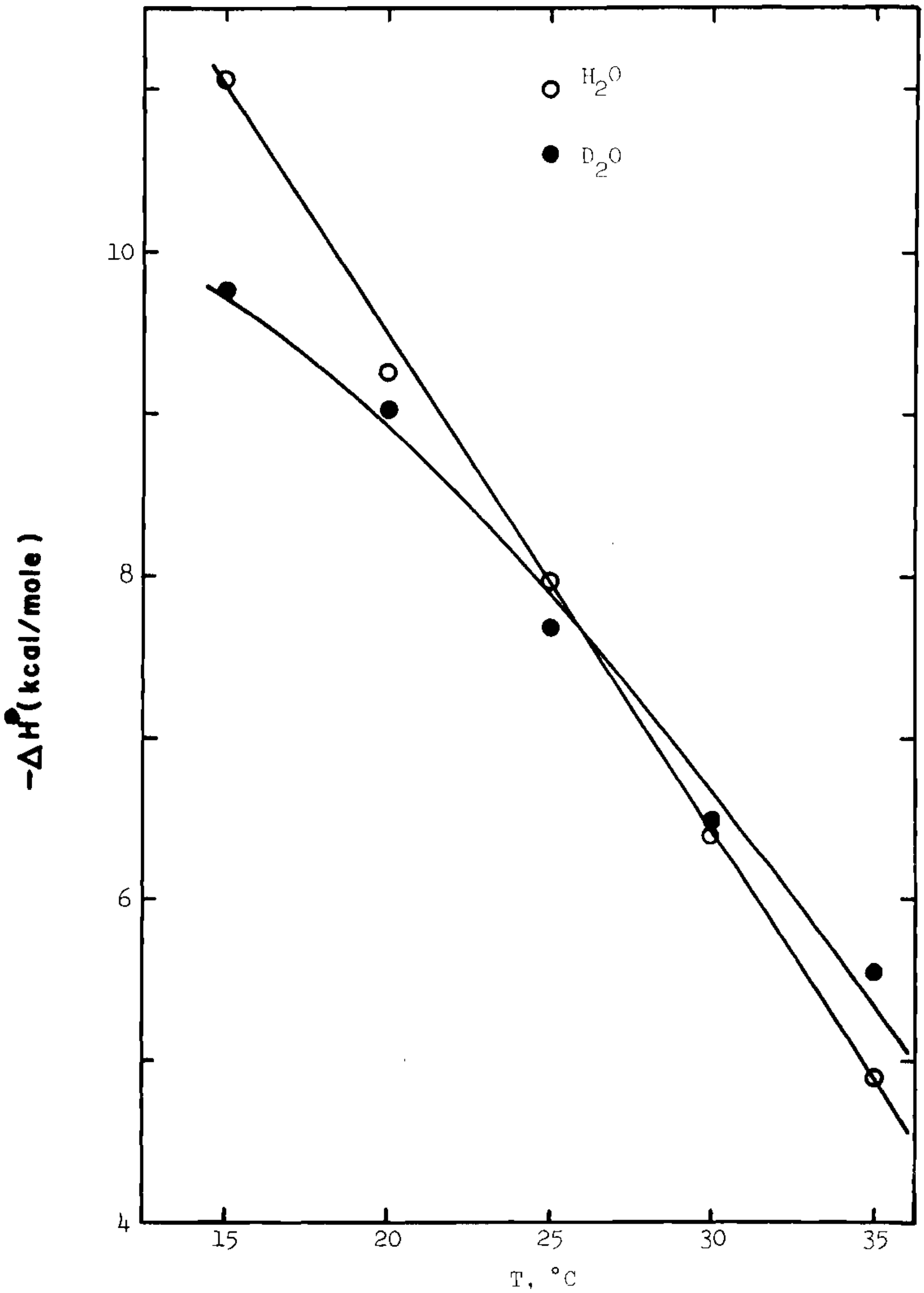

Figure 7. $-\Delta H^{o}$ of Ethylbenzene in H_2O and D_2O as a Function of Temperature

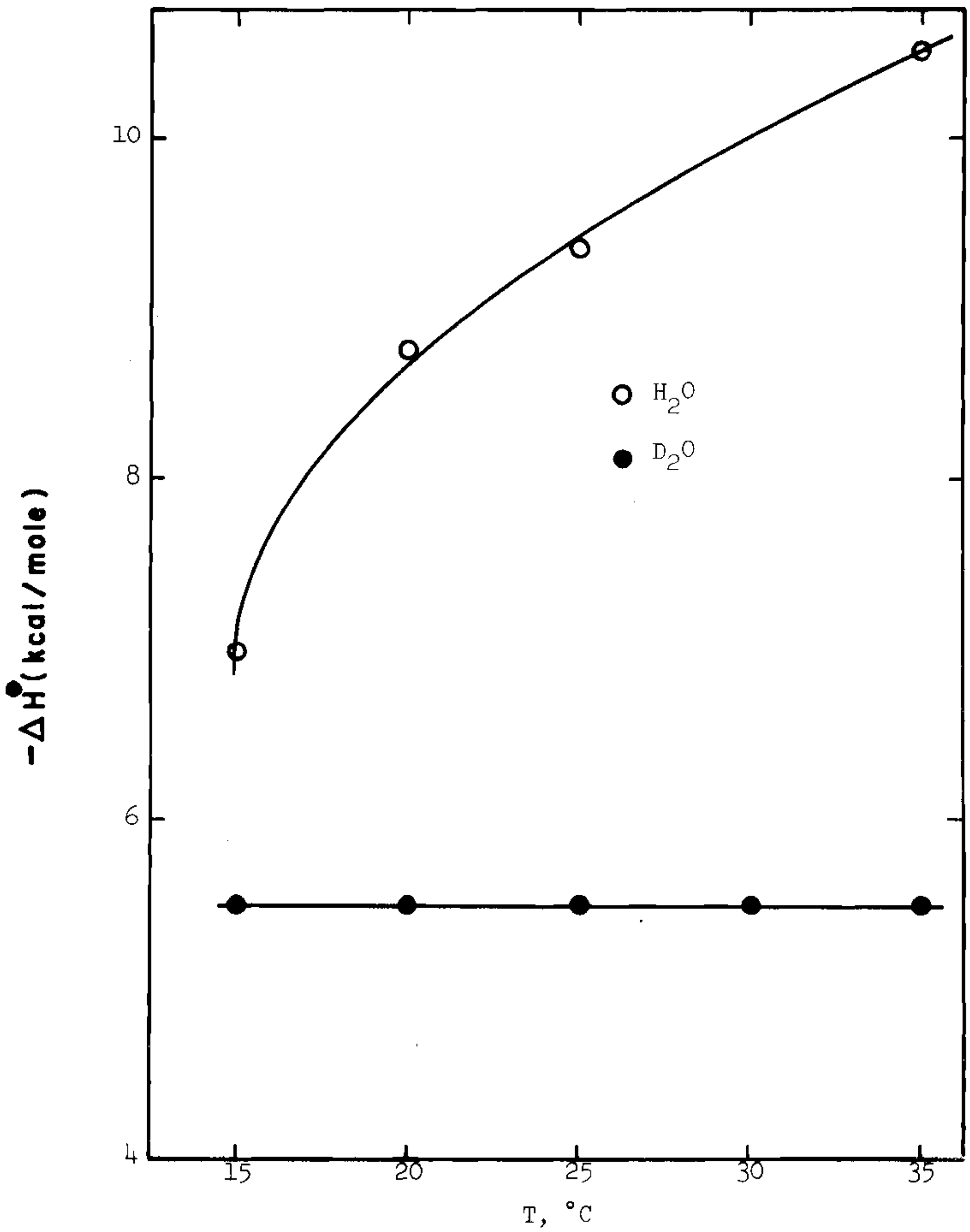

Figure 8. $-\Delta H^{\circ}$ of Isopropylbenzene in H_2O and D_2O as a Function of Temperature

The values of the heat capacity change were found from the slopes of the standard enthalpy change-temperature curves. The values of heat capacity change were also plotted against temperature for each hydrocarbon and are shown in Figures 9-12.

The standard entropy change, ΔS^{o}, can be calculated from the following equation.

$$\Delta S^{o} = \frac{\Delta H^{o}}{T} - \frac{\Delta G^{o}}{T} \tag{7}$$

The values of ΔS^{o} versus T are shown in Figures 13-16.

Combined plots of the same thermodynamic properties of different hydrocarbons in H_2O and in D_2O are shown in Figures 17-22 in order to give a comparison between the thermodynamic properties of different hydrocarbons.

The thermodynamic properties of each of these four hydrocarbons in H_2O and in D_2O at different temperatures are listed in Tables 5-7.

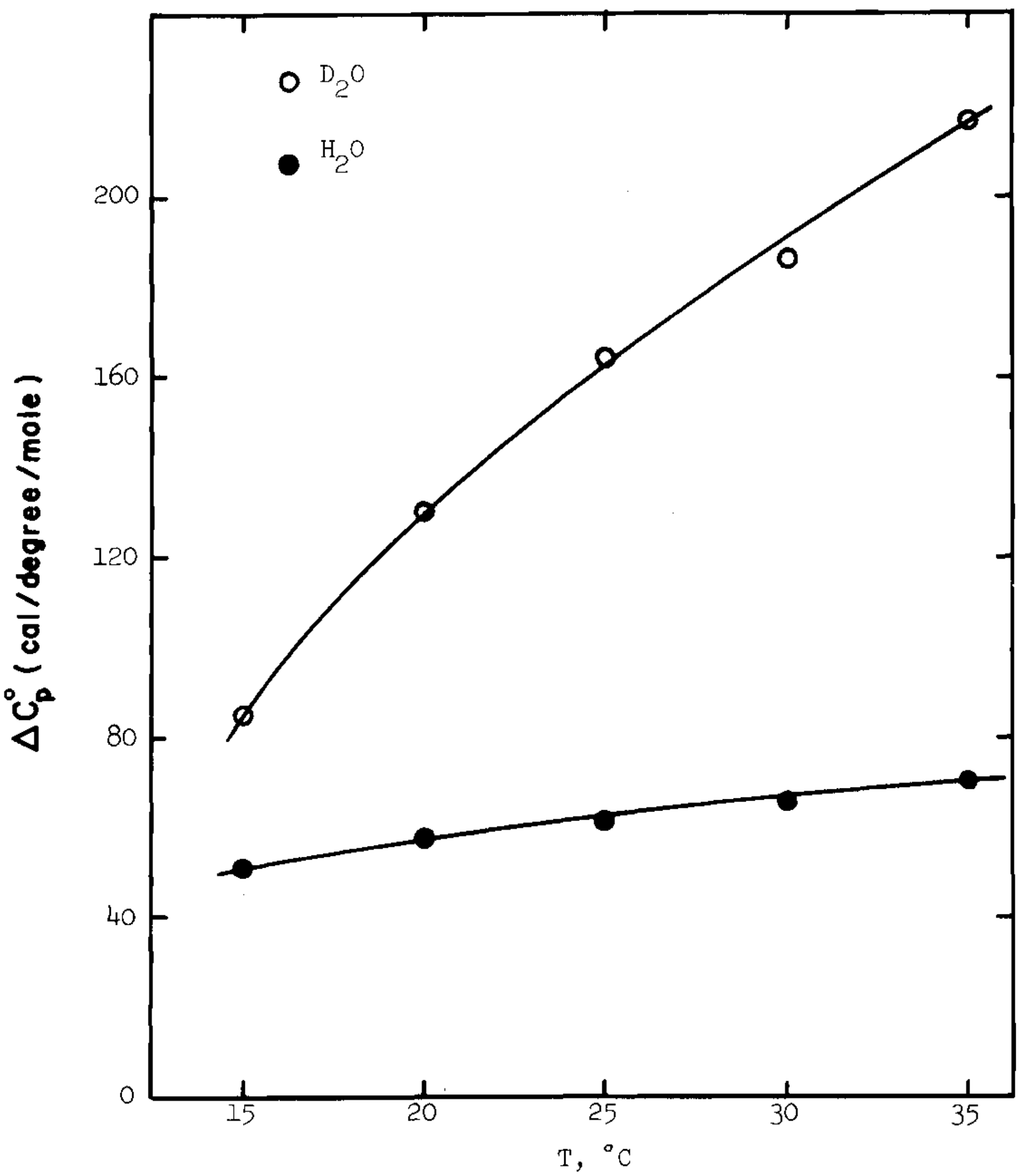

Figure 9. ΔC_p^o of Benzene in H_2O and D_2O as a Function of Temperature

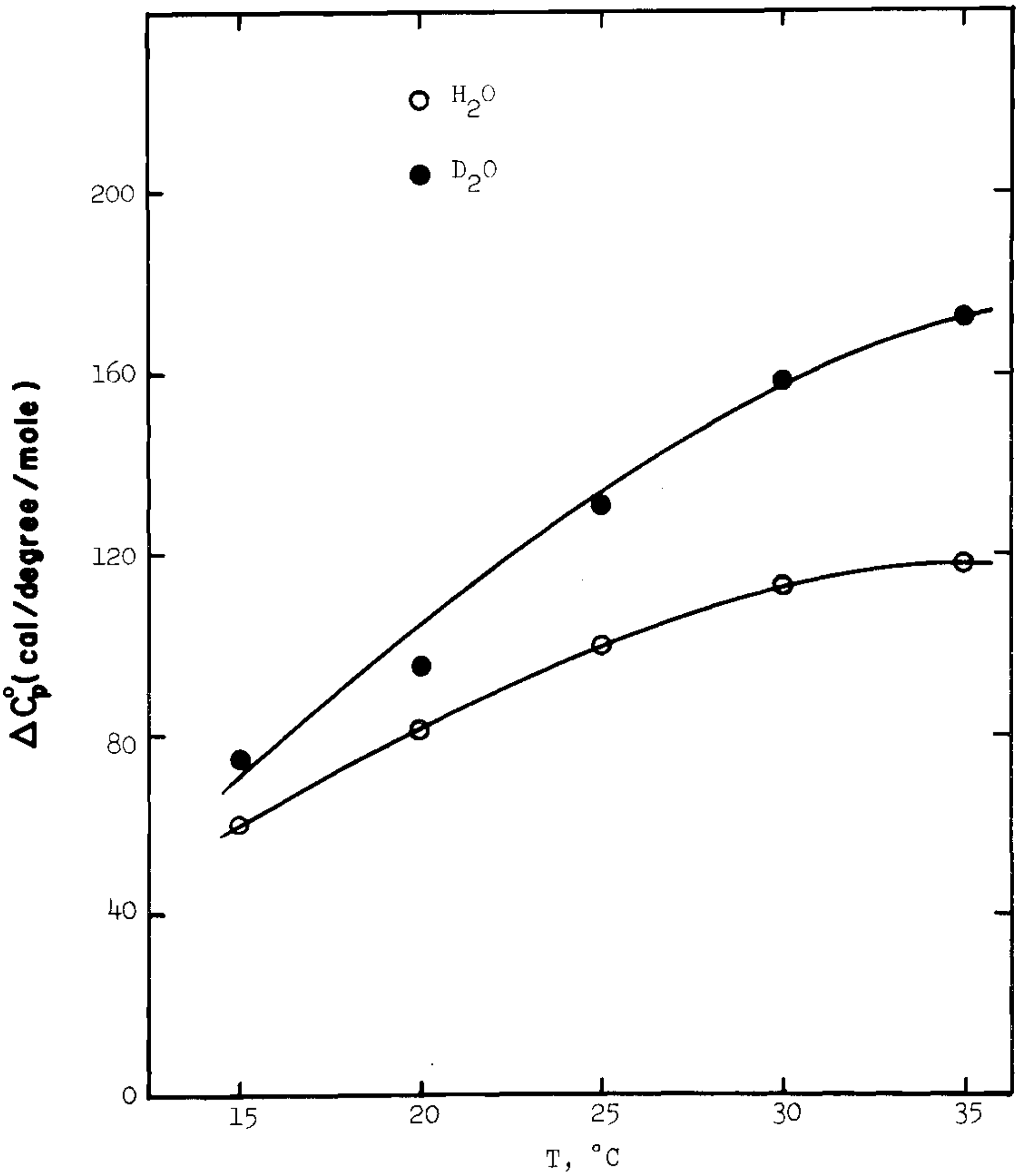

Figure 10. ΔC_p^o of Toluene in H_2O and D_2O as a Function of Temperature

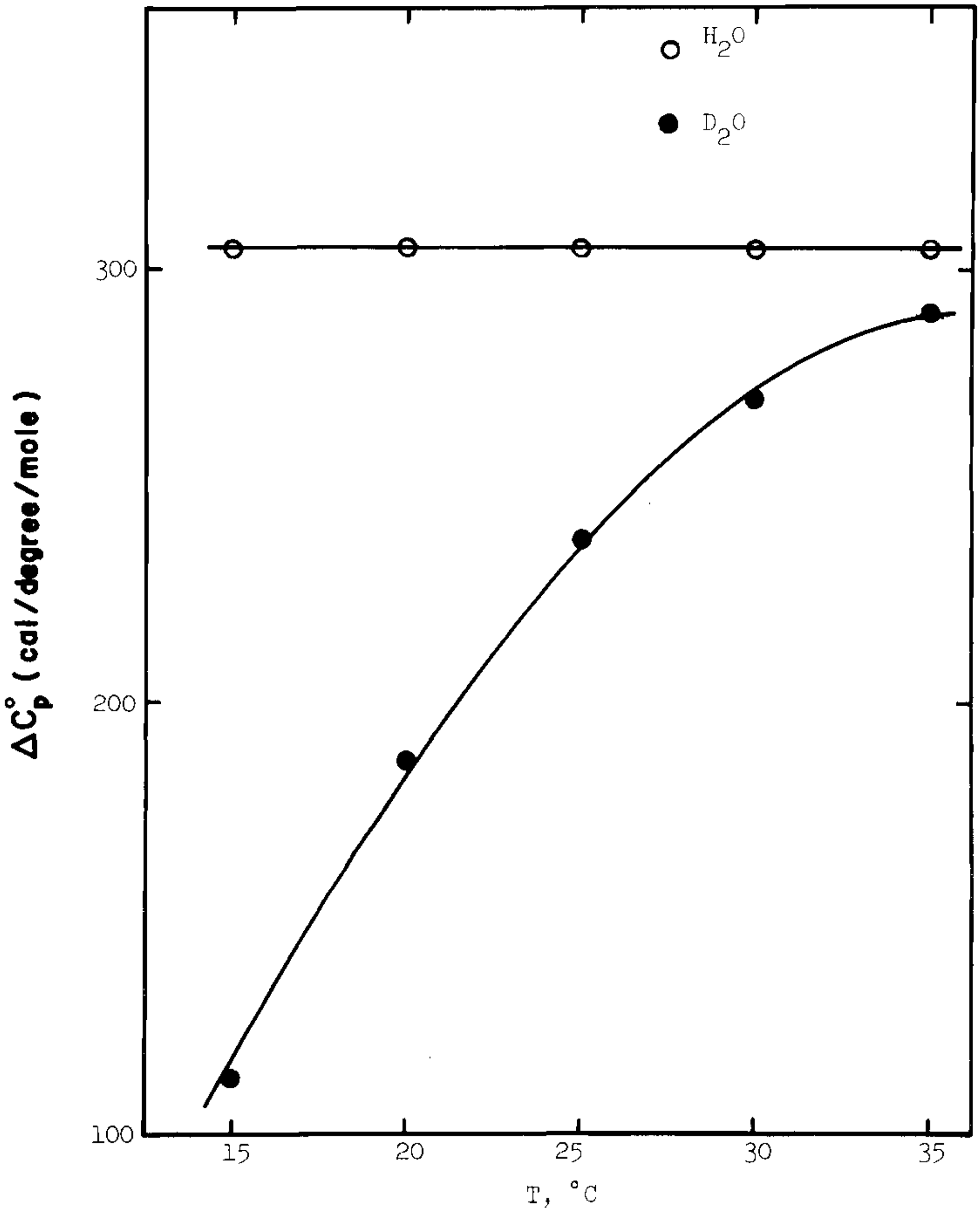

Figure 11. ΔC_p^o of Ethylbenzene in H_2O and D_2O as a Function of Temperature

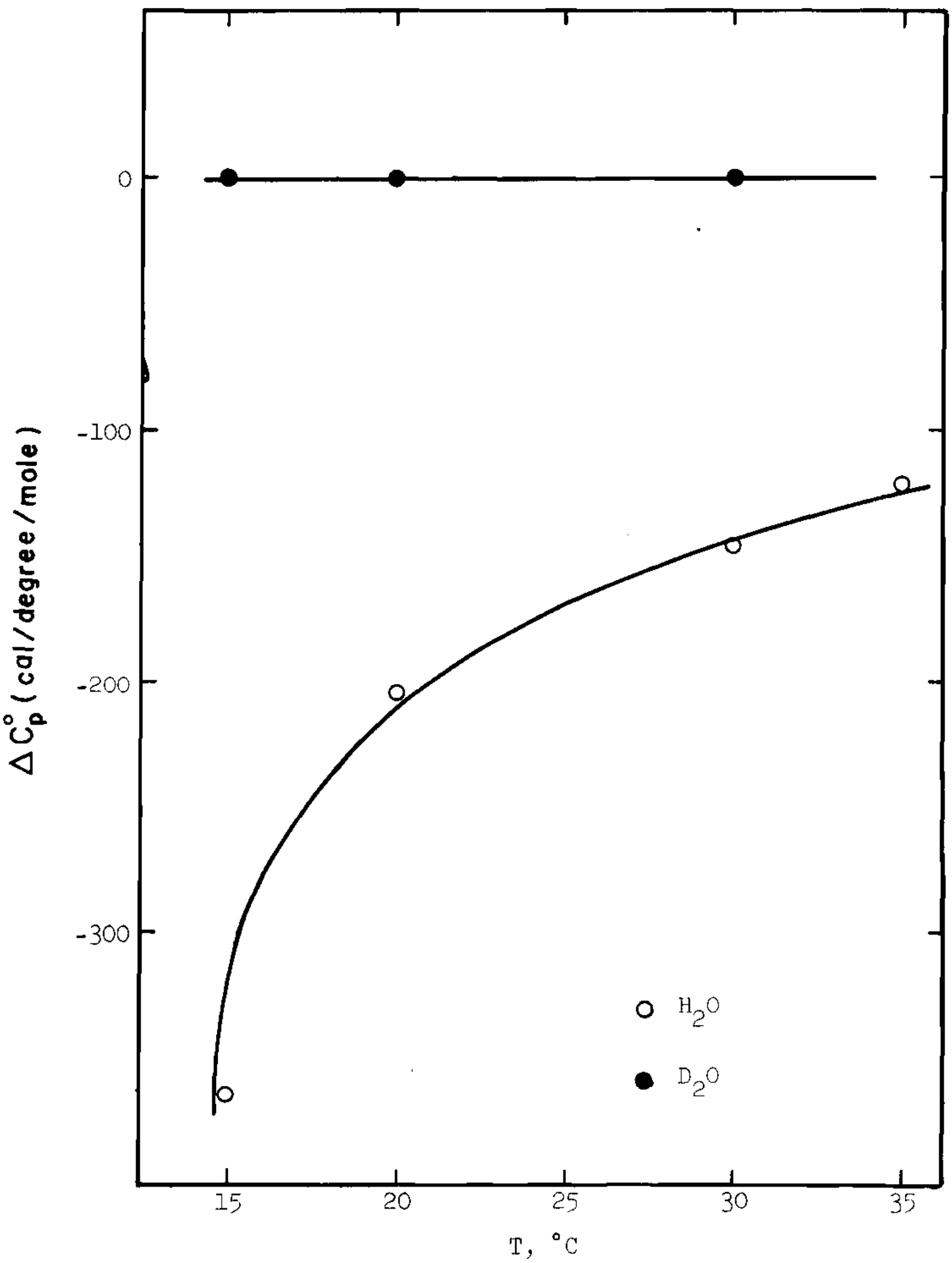

Figure 12. ΔC_p^o of Isopropylbenzene in H_2O and D_2O as a Function of Temperature

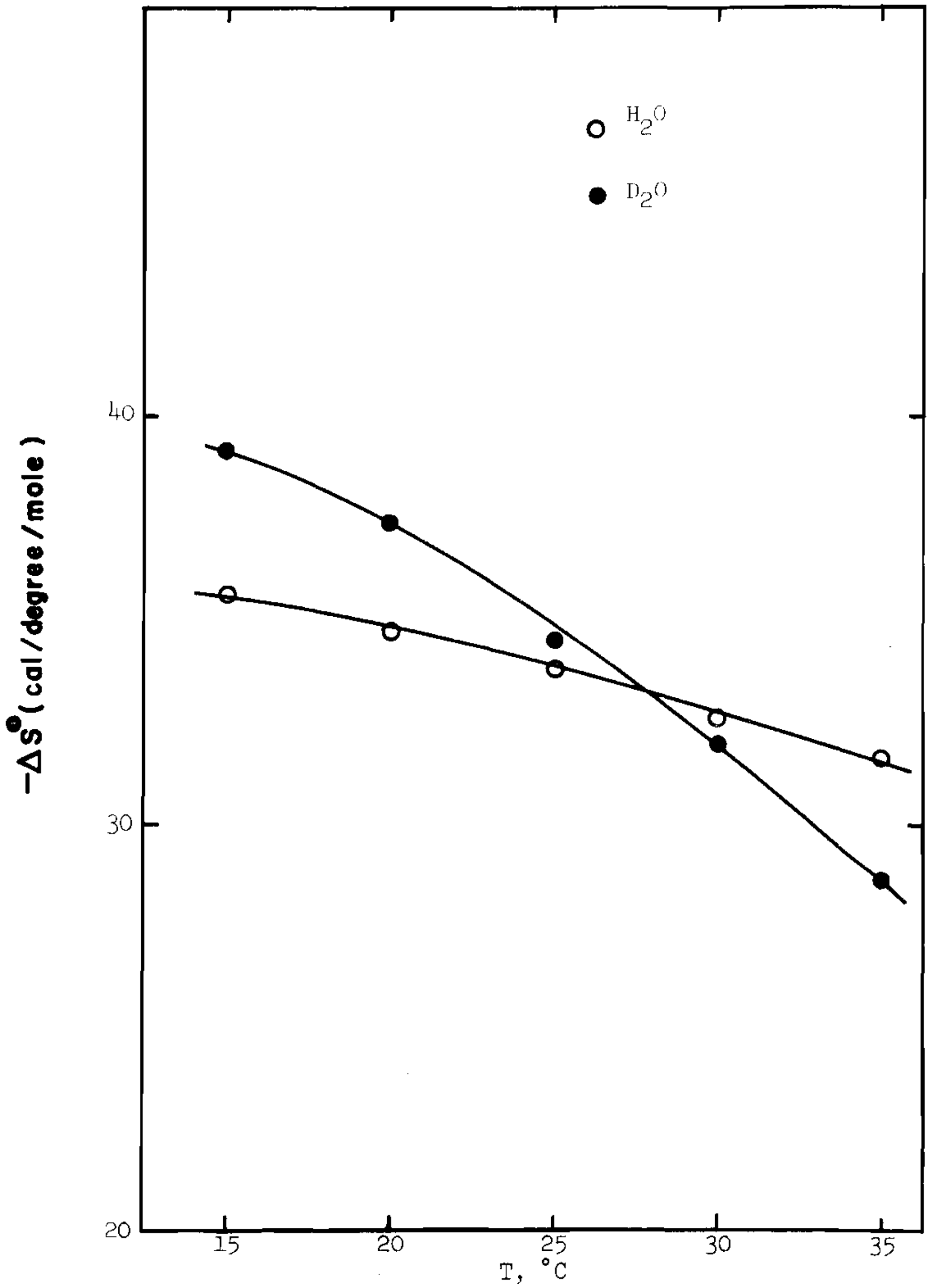

Figure 13. $-\Delta S^{\circ}$ of Benzene in H_2O and D_2O as a Function of Temperature

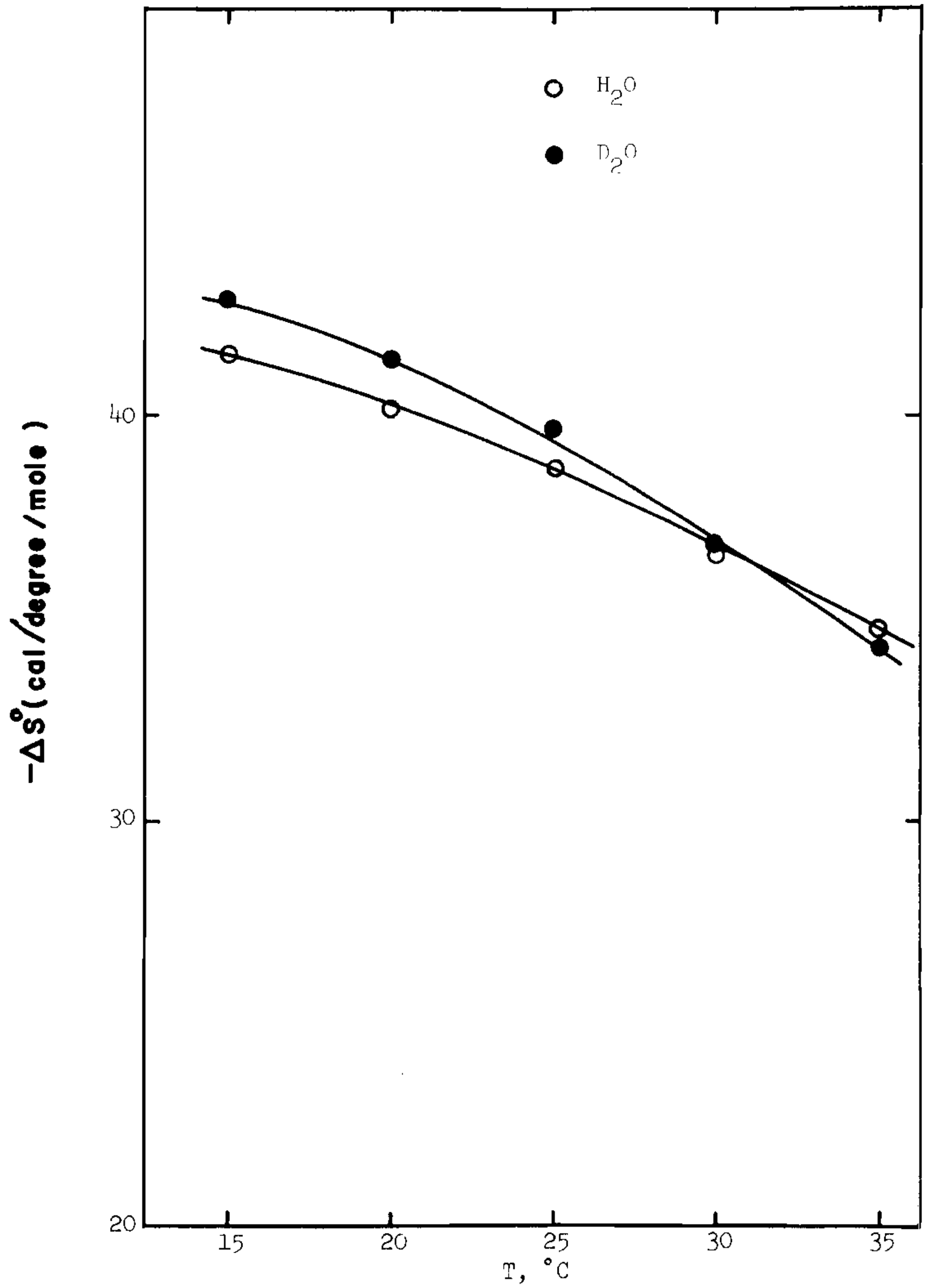

Figure 14. $-\Delta S^{o}$ of Toluene in H_2O and D_2O as a Function of Temperature

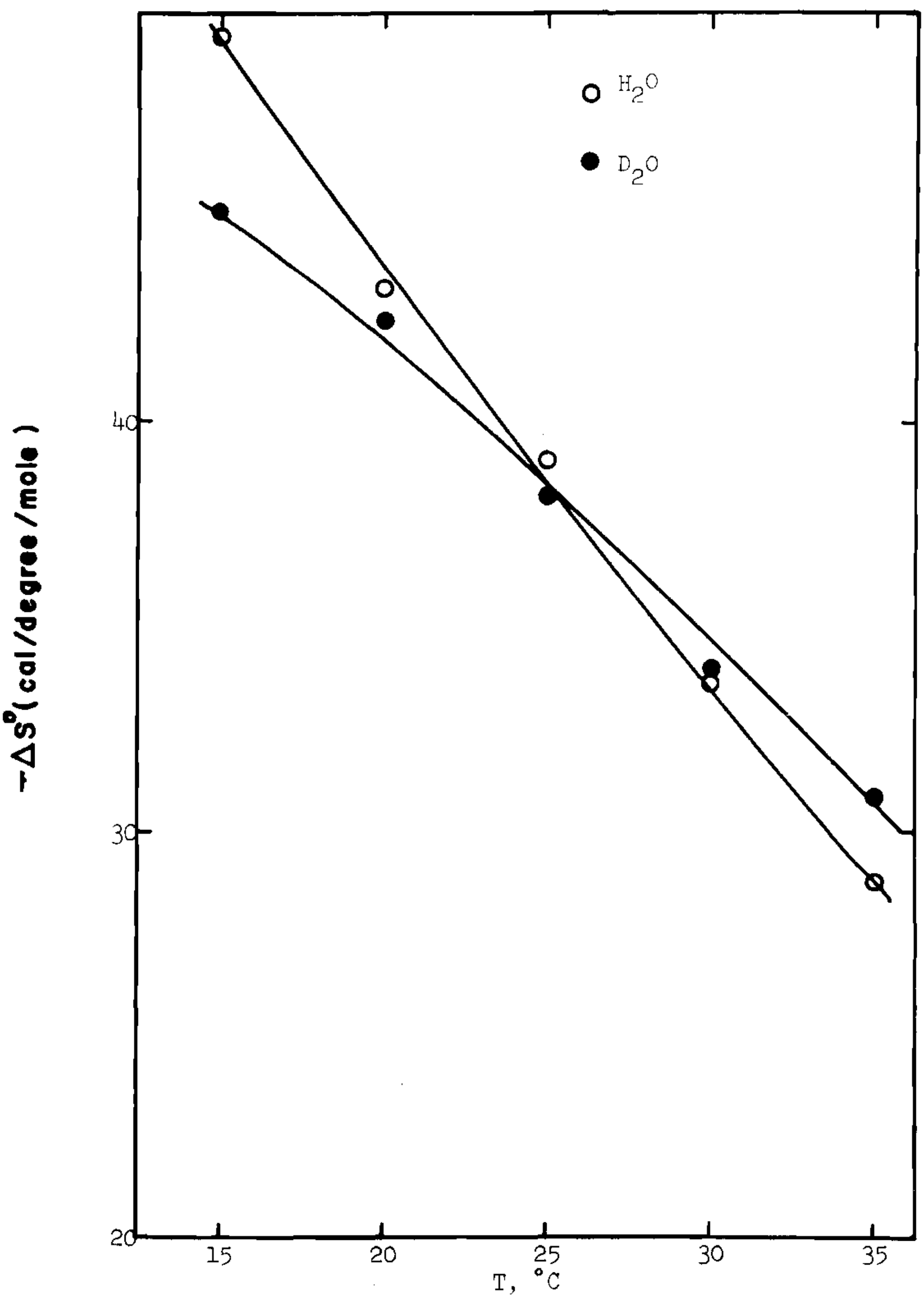

Figure 15. -ΔS° of Ethylbenzene in H_2O and D_2O as a Function of Temperature

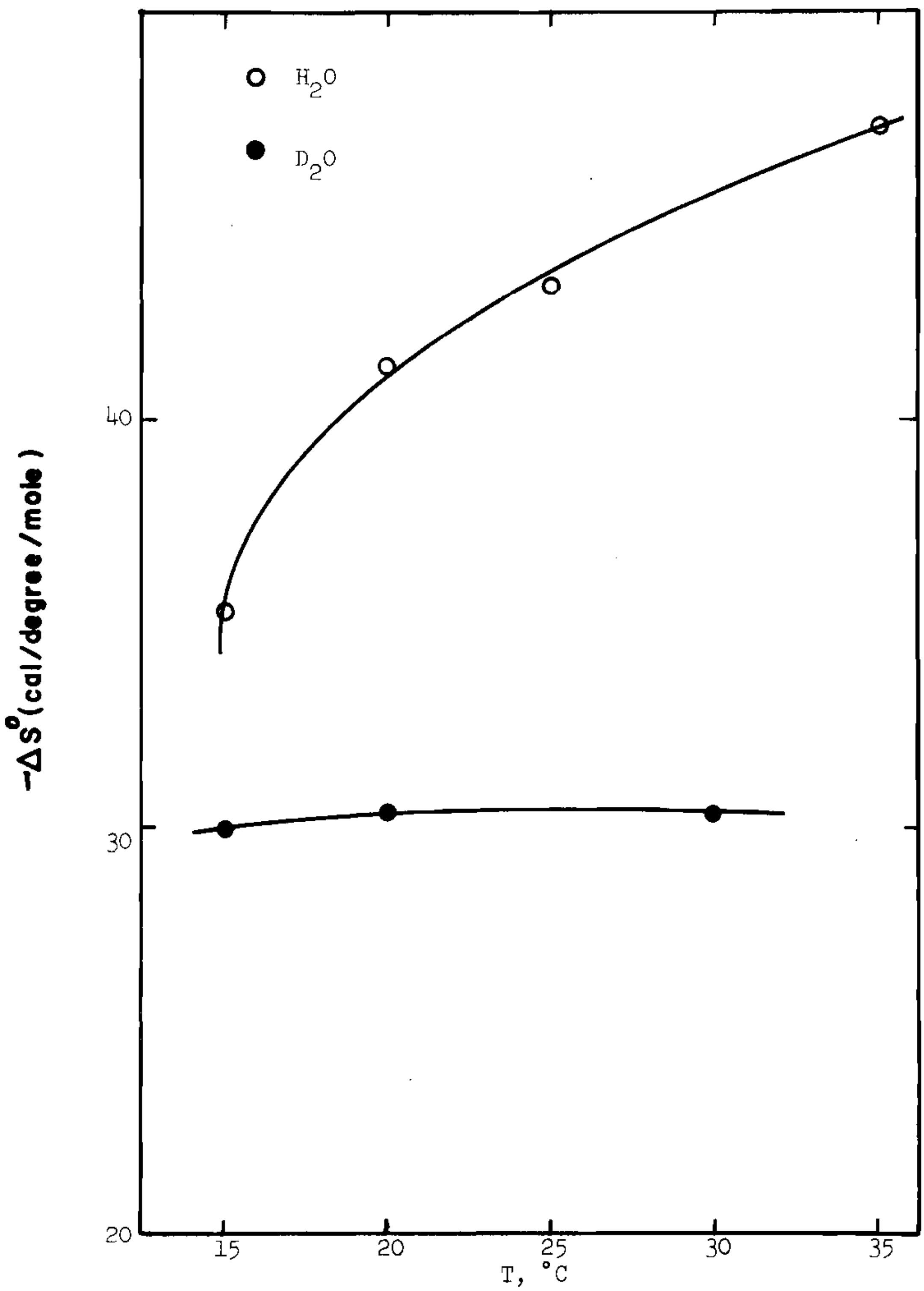

Figure 16. $-\Delta S^{o}$ of Isopropylbenzene in H_2O and D_2O as a Function of Temperature

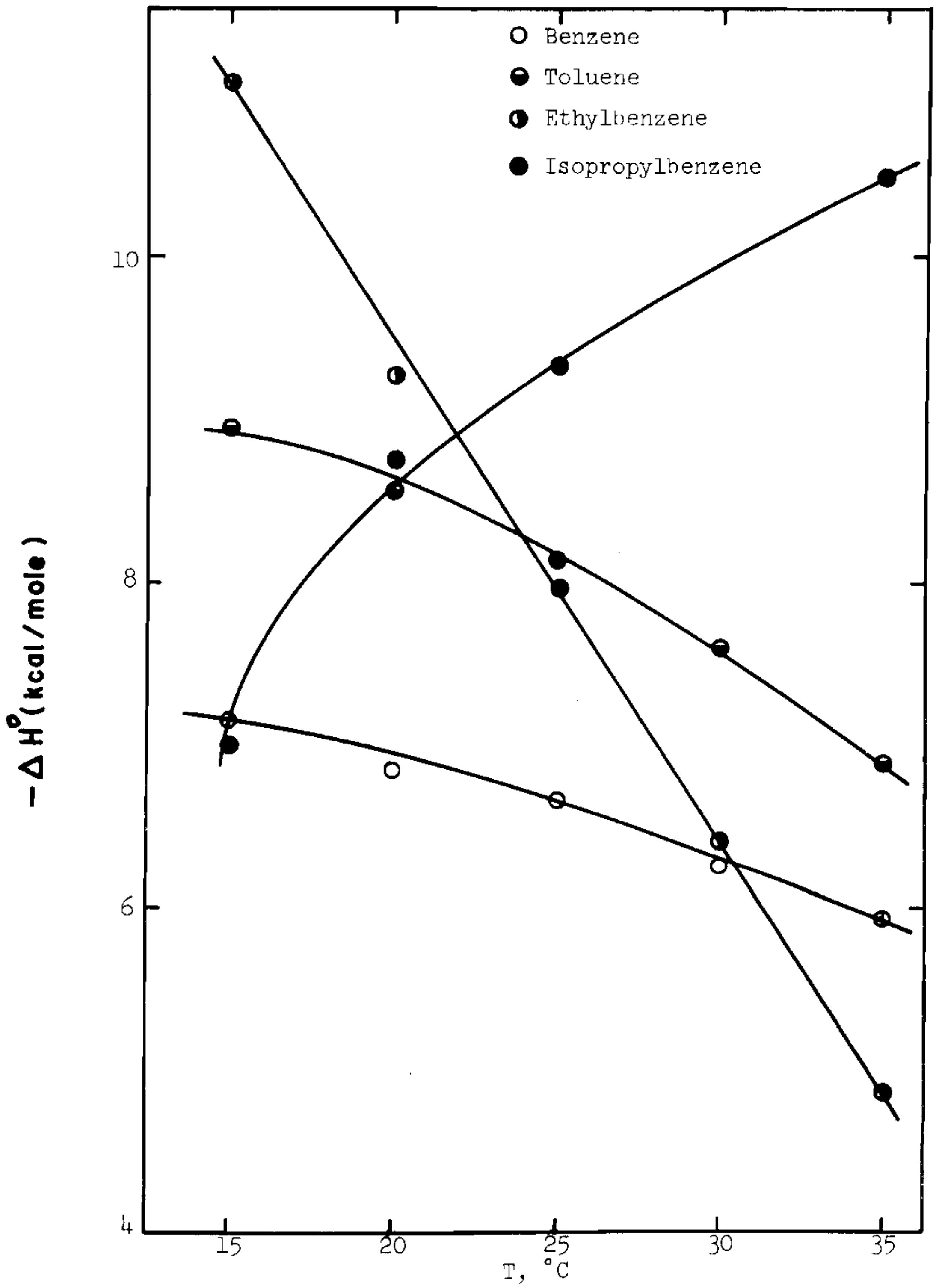

Figure 17. $-\Delta H^{\circ}$ of Hydrocarbons in H_2O as a Function of Temperature

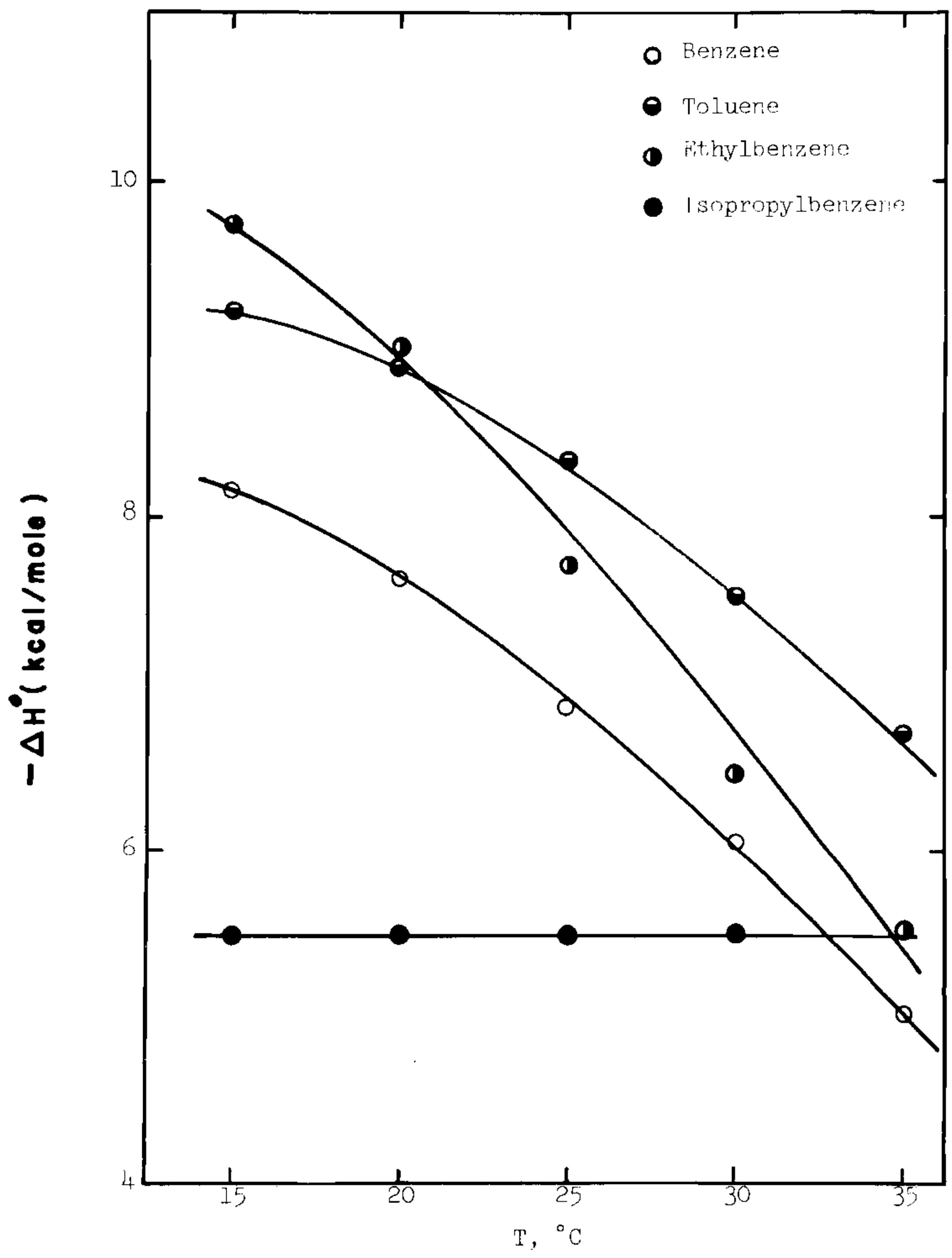

Figure 18. $-\Delta H^{\circ}$ of Hydrocarbons in D_2O as a Function of Temperature

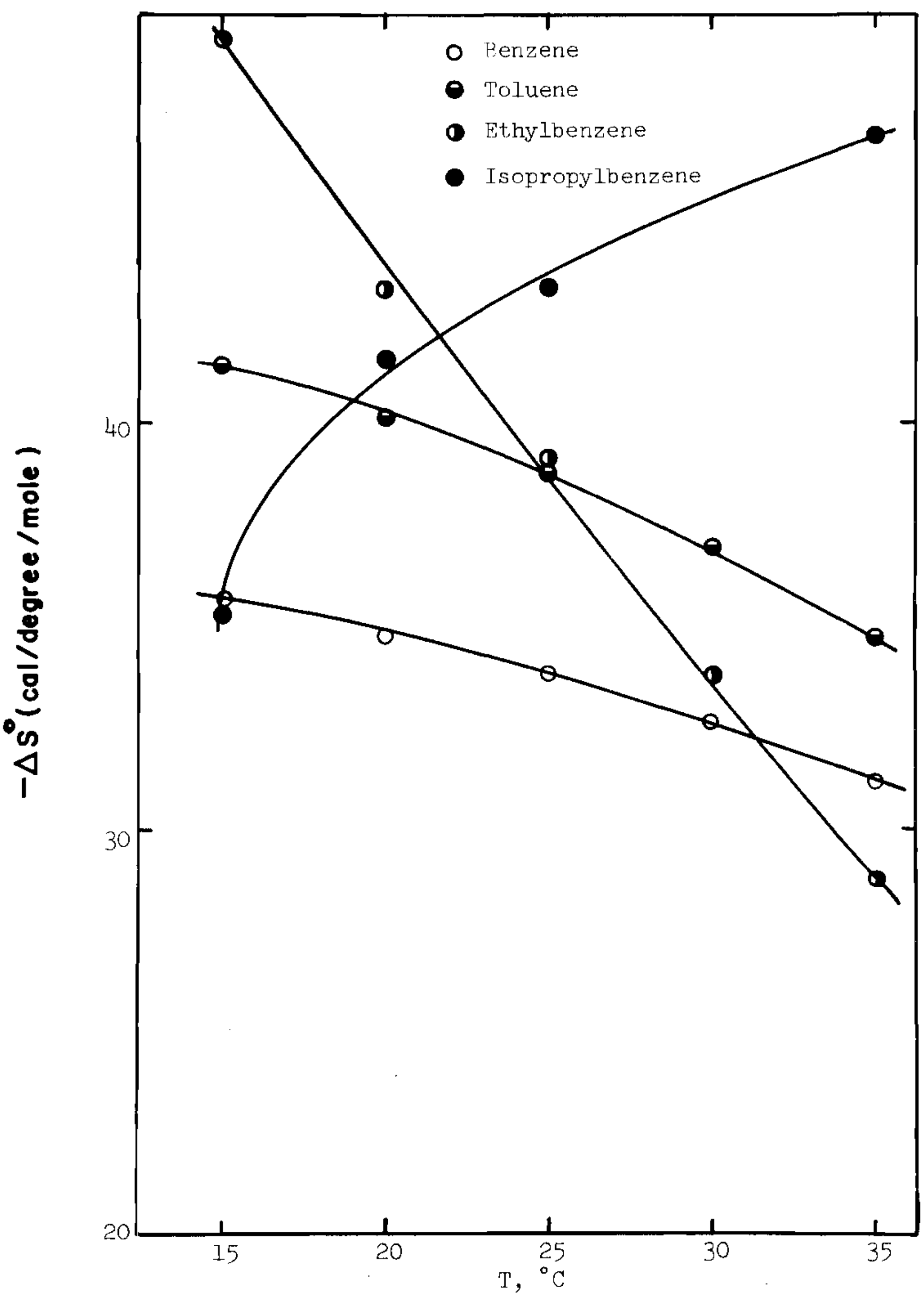

Figure 19. $-\Delta S^{\circ}$ of Hydrocarbons in H_2O as a Function of Temperature

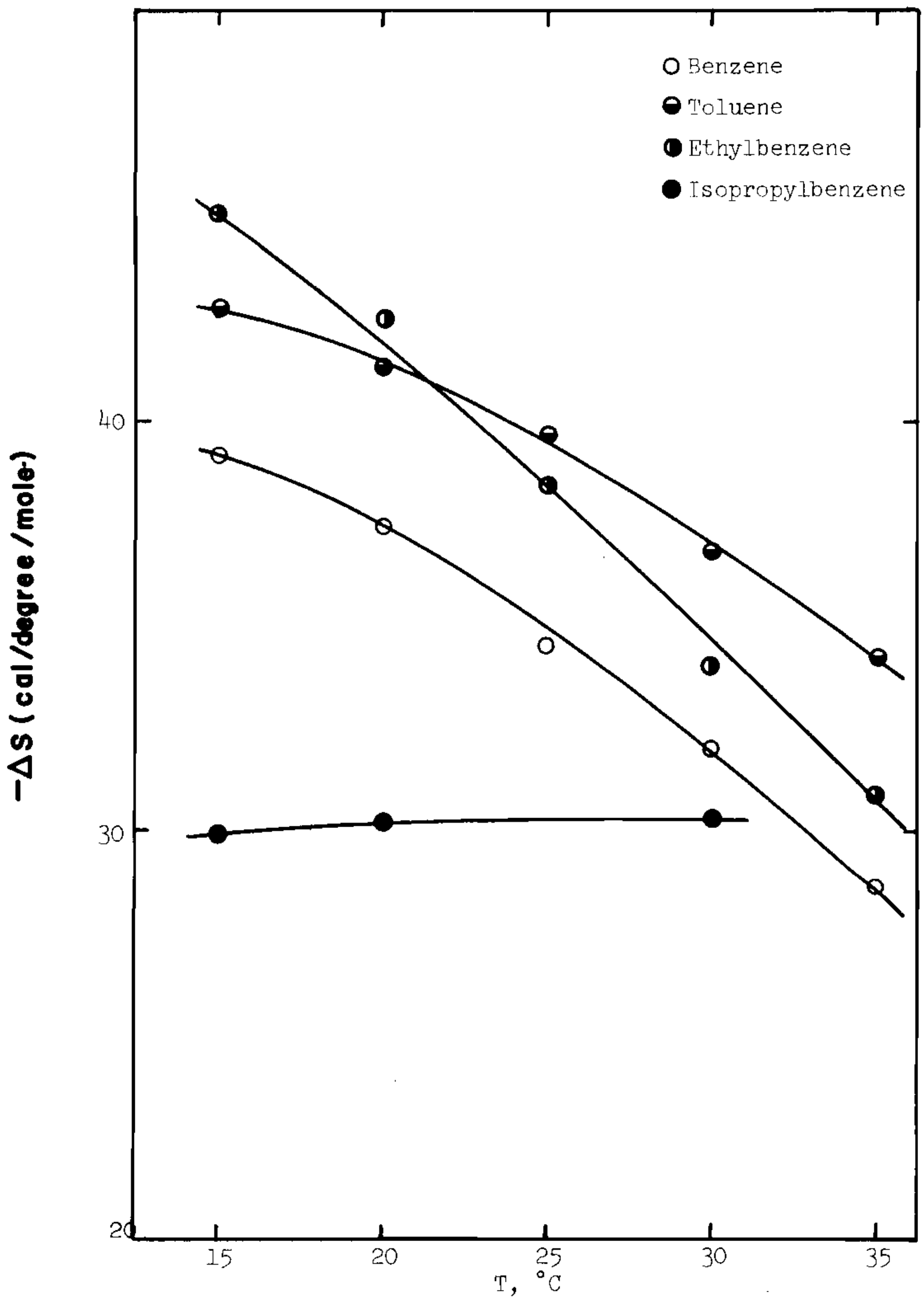

Figure 20. $-\Delta S^o$ of Hydrocarbons in D_2O as a Function of Temperature

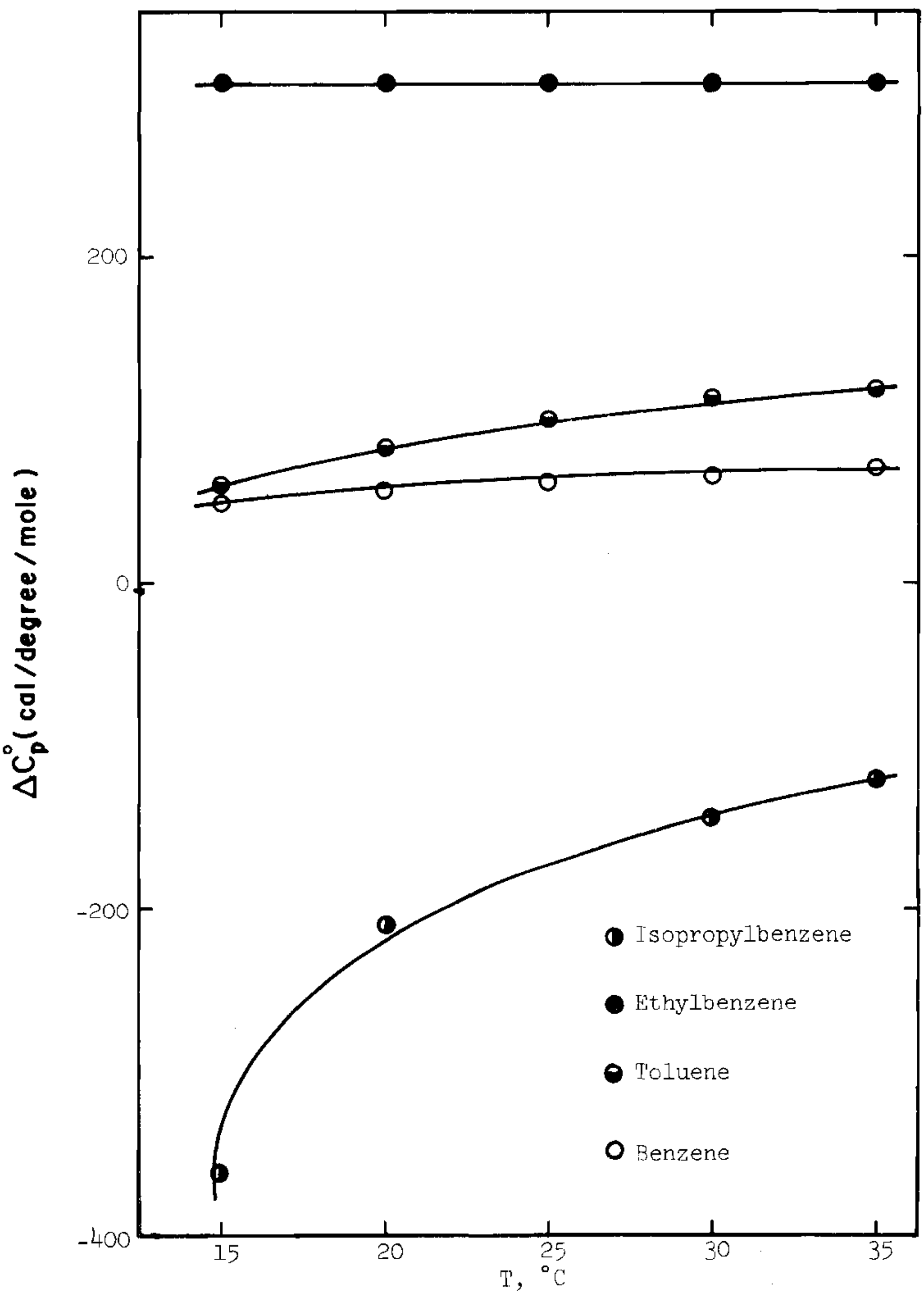

Figure 21. ΔC_p^o of Hydrocarbons in H_2O as a Function of Temperature

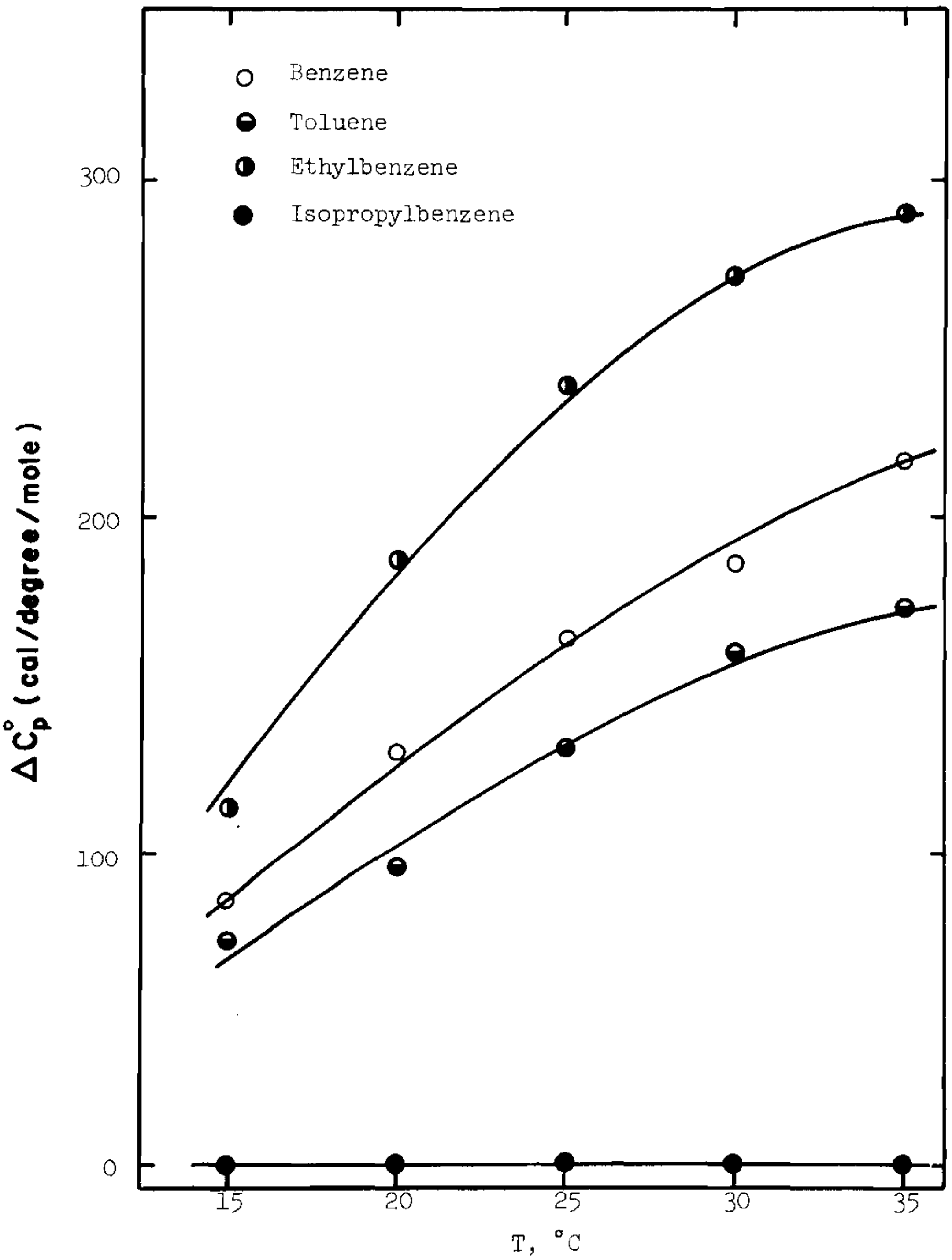

Figure 22. ΔC_p^o of Hydrocarbons in D_2O as a Function of Temperature

Table 5. $-\Delta H^{o}$, Kcal/mole, of Hydrocarbons in H_2O and D_2O

Hydrocarbons	Solvent	T, °C				
		15	20	25	30	35
Benzene	H_2O	7.145	6.880	6.670	6.250	5.940
		8.43	7.8 [3]	7.5 [3]	7.2 [3]	6.8 [3]
	D_2O	8.163	7.634	6.849	6.042	5.025
Toluene	H_2O	8.930	8.560	8.130	7.595	6.900
				8.85 [16]		
	D_2O	9.200	8.800	8.333	7.500	6.707
Ethylbenzene	H_2O	11.05	9.260	7.970	6.390	4.870
				10.03 [16]		
	D_2O	9.740	9.010	7.690	6.450	5.520
Isopropylbenzene	H_2O	7.000	8.750	9.340		10.50
	D_2O	5.490	5.490	5.490		5.490

Table 6. ΔC_p^o, cal/degree/mole, of Hydrocarbons in H_2O and D_2O

Hydrocarbons	Solvent	T, °C				
		15	20	25	30	35
Benzene	H_2O	50.5	57.8	61.6	65.6	70.3
		45 [3]	75 [3]	90 [3]	75 [3]	50 [3]
	D_2O	85.1	130	164	186	217
Toluene	H_2O	60.3	81.4	100	113	118
	D_2O	74.1	95.2	131	159	173
Ethylbenzene	H_2O	305	305	305	305	305
	D_2O	113	187	238	270	290
Isopropylbenzene	H_2O	-362	-204	-144	---	-120
	D_2O	---	---	---	---	---

Table 7. $-\Delta S^{\circ}$, cal/degree/mole, of Hydrocarbons in H_2O and D_2O (P = 760 Torr)

Hydrocarbons	Solvent	T, °C				
		15	20	25	30	35
Benzene	H_2O	35.6	34.7	33.8	32.6	31.6
		39.2[3]	38.2[3]	36.2[3]	35.2[3]	33.5[3]
	D_2O	39.2	37.4	34.5	32.0	28.6
Toluene	H_2O	41.5	40.2	38.7	36.9	34.7
				40.9[16]		
Ethylbenzene	H_2O	49.4	43.3	39.1	33.7	28.7
				45.2[16]		
	D_2O	45.1	42.5	38.3	34.0	30.9
Isopropylbenzene	H_2O	35.3	41.3	43.3	----	47.1
	D_2O	30.0	30.3	----	30.3	----

CHAPTER IV

CONCLUSIONS

The solubilities of all four hydrocarbons were found to be higher in H_2O than in D_2O in this investigation, no matter whether a molal, molar, or mole fraction basis was used.

The standard free energy changes for benzene, toluene, and ethylbenzene calculated from $-RT\ln\frac{X_2}{P_2}$ were lower than the values of Franks, *et al.*,[3] and Herington.[16] The standard enthalpy changes of benzene at various temperatures were found to be lower than the values from Franks, *et al*. The standard enthalpy changes for toluene and ethylbenzene at 25°C were also smaller than Herington's work. The standard entropy changes for toluene, benzene, and ethylbenzene, using the same standard state, were lower than those of Herington. The enthalpy change-temperature curves and the entropy change-temperature curves were compared with Franks' work. It was found that there were no maxima in the curves for any of these hydrocarbons, whereas Franks' work indicated the existence of maxima near 20°C. For benzene and toluene, the standard enthalpy changes and the standard entropy changes in D_2O were higher at the higher temperature than the standard enthalpy changes and the standard entropy changes in H_2O; at the lower temperature the opposite behavior was observed. The standard enthalpy change and the standard entropy change values exhibit the opposite behavior for ethylbenzene from that observed for benzene and toluene. For isopropylbenzene, the standard enthalpy change and the standard entropy change values for D_2O solutions were lower than the corresponding values for H_2O solutions at all temperatures investigated, and in D_2O the standard enthalpy changes and the standard entropy changes were independent of temperature over the temperature range studied here.

The heat capacity changes for benzene and toluene in H_2O were higher than in D_2O at all temperatures. For isopropylbenzene, the values of the heat capacity change in D_2O were zero (independent of temperature) and in H_2O were negative. The heat capacity changes for ethylbenzene in H_2O were higher than in D_2O. Generally, the values of heat capacity changes increased as temperature increased except for those of ethylbenzene in H_2O and isopropylbenzene in D_2O. In the last two systems, the heat capacity changes were independent of temperature.

Intuitively, the results for the isopropylbenzene system seem questionable, and this system especially warrants further investigation.

CHAPTER V

RECOMMENDATIONS

Flame-ionization gas chromatography is an excellent way to determine the concentration of compounds in water which are only slightly soluble. The following modifications are suggested in order to improve the experiment done in this work.

(1) A Teflon cap or a cap made of some other material that will not swell when in contact with the hydrocarbon is recommended as a stopper for the sample bottle.

(2) A lower column temperature, about 120°C for ethylbenzene and 130°C for isopropylbenzene, in order to minimize the background current. It is also suggested that the column temperature be 80°C for benzene.

(3) A liquid with a shorter retention time than that of n-hexane is recommended as the solvent in preparing the calibration solutions for these four hydrocarbons or hydrocarbons with similar retention times.

(4) If n-hexane is used as the solvent for these hydrocarbons, a lower flow rate is suggested.

(5) Since the reproducibility of the planimeter is not high, a large amount of sample or low attenuation on the gas chromatograph is suggested to obtain larger areas and hence a lower percentage error in the area measurement. Using a large number of samples is also recommended.

APPENDIX

Table 8. Solubility Data of Hydrocarbons in H_2O and D_2O at 10°C in Terms of Peak Area

Hydrocarbon	Benzene		Toluene		Ethylbenzene		Isopropylbenzene	
Solvent	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
Attenuation	400		100		64		32	
	72	61	109	87	71	49	50	35
	77	61	106	87	71	57	45	47
	70	63	101	91	57	51	51	41
	70	64	108	78	63	53	51	41
	74	63	103	79	60	54	53	49
	74	62	99	88	60	59	47	39
	70	75	101		61	55		
	69	75	90			50		
	71	73	90			53		
	71					50		
						48		
						49		
Average	71.8	66.3	100.1	83.7	63.3	52.3	49.5	42.6

Carrier gas flow rate = N_2, 75 cc/min
H_2 gas flow rate = 15 cc/min
Air flow rate = 75 cc/min
Amount of sample injected = 3 μl

Table 9. Solubility Data of Hydrocarbons in H_2O and D_2O at 15°C in Terms of Peak Area

Hydrocarbon	Benzene		Toluene		Ethylbenzene		Isopropylbenzene	
Solvent	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
Attenuation	400		100		64		32	
	75	72	92	71	59	51	63	53
	74	70	97	84	55	50	51	50
	73	67	95	79	59	45	51	55
	72	74	94	68	54	53	49	52
	77	70	86	78	62	62	62	
	76	64	89	78	59	62	63	
		73	99		63	51	61	
		69	97		59	49	46	
		71	85			52	51	
		72	97					
		73	100					
			86					
			91					
			91					
Average	74.5	70.5	94.5	76.4	59.8	52.8	56.4	52.5

Carrier gas flow rate = N_2, 75 cc/min
H_2 gas flow rate = 15 cc/min
Air flow rate = 75 cc/min
Amount of sample injected = 3 μl

Table 10. Solubility Data of Hydrocarbons in H_2O and D_2O at 20°C in Terms of Peak Area

Hydrocarbon	Benzene		Toluene		Ethylbenzene		Isopropylbenzene	
Solvent	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
Attenuation	400		100		64		32	
	74	66	96	86	56	54	65	55
	82	70	96	87	55	55	57	59
	82	75	99	78	57	55	64	60
	79	71	97	82	58	63	61	61
	80	65	102	77	61	54	58	62
	79	75	100	82	53	54	65	60
	82	76	89	84	67	52	59	57
	77	73	87	80	52	62	55	55
	78	66	90	83		56	55	55
	87	68	95					
	84	70	88					
	85	67						
	87	77						
	82	74						
Average	81.2	70.9	94.5	82.1	57.4	56.1	60.0	58.2

Carrier gas flow rate = N_2, 75 cc/min
H_2 gas flow rate = 15 cc/min, Air flow rate = 75 cc/min
Column temperature = 150°C for Benzene, Toluene
= 100°C for Ethylbenzene, Isopropylbenzene
Amount of sample injected = 3 µl

Table 11. Solubility Data of Hydrocarbons in H_2O and D_2O at 25°C in Terms of Peak Area

Hydrocarbon	Benzene		Toluene		Ethylbenzene		Isopropylbenzene	
Solvent	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
Attenuation	400		100		64		32	
	95	67	103	81	54	52	68	
	90	71	98	92	56	49	63	
	84	77	106	97	59	53	67	
	86	76	95	78	55	55	70	
	78	73	89	80	58	50	61	
	84	71	94	86		62	56	
	96	78	99	92		45		
	81	71	96	77		55		
	88	74	90	93				
	83	75	92					
		76	101					
		69	105					
		67	97					
		68						
		68						
		70						
Average	86.5	71.6	97.3	86.2	56.4	52.6	64.1	

Carrier gas flow rate = N_2, 75 cc/min

H_2 gas flow rate = 15 cc/min

Air flow rate = 75 cc/min

Amount of sample injected = 3 μl

Table 12. Solubility Data of Hydrocarbons in H_2O and D_2O at 30°C in Terms of Peak Area

Hydrocarbon	Benzene		Toluene		Ethylbenzene		Isopropylbenzene	
Solvent	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
Attenuation	400		100		64		32	
	83	71	98	99	67	66		76.5
	83	70	99	97	60	66		78.0
	77	70	107	100	67	51		81.0
	79	69	107	94	62	67		81.0
	79	67	108	96	66	68		85.5
	79	68	106	89	61	52		78.0
	89	68	98	86	61	57		82.5
	85	72	105	84	61	60		73.5
	88	73	106	83	68	69		76.5
	76	75	106		70			
	85	79	98					
	82	68						
	83	77						
	87	78						
		79						
Average	82.8	71.9	103.5	92.0	64.7	61.8		79.2

Carrier gas flow rate = N_2, 75 cc/min
H_2 gas flow rate = 15 cc/min
Air flow rate = 75 cc/min
Amount of sample injected = 3 µl

Table 13. Solubility Data of Hydrocarbons in H_2O and D_2O at 35°C in Terms of Peak Area

Hydrocarbon	Benzene		Toluene		Ethylbenzene		Isopropylbenzene	
Solvent	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
Attenuation	400		100		64		32	
	86	73	93	97	76	66	78	
	86	79	109	92	81	71	62	
	88	74	112	95	83	69	76	
	88	80	96	97	64	69	60	
	89	79	101	94	70	69	75	
	89	76	96	95		67	74	
	89	74	96	90		72	64	
		78	109	90		63		
		82	111	89		79		
		75	104	90				
		76						
		79						
		81						
Average	87.9	77.4	102.7	92.9	77.5	69.4	69.9	

Carrier gas flow rate = N_2, 75 cc/min
H_2 gas flow rate = 15 cc/min
Air flow rate = 75 cc/min
Amount of sample injected = 3 μl

Table 14. Solubility Data of Hydrocarbons in H_2O and D_2O at 40°C in Terms of Peak Area

Hydrocarbon	Benzene		Toluene		Ethylbenzene		Isopropylbenzene	
Solvent	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
Attenuation	400		100		64		32	
	109	86	124	89	107	88		
	92	86	111	104	79	74		
	90	89	111	101	96	78		
	96	89	121	90	90	80		
	102	98	98	100	100			
	100	98	108					
	96	89						
Average	98.0	90.4	112.7	96.7	95.0	80.0		

Carrier gas flow rate = N_2, 75 cc/min
H_2 gas flow rate = 15 cc/min
Air flow rate = 75 cc/min
Amount of sample injected = 3 μl

Table 15. Calibration Curve, Benzene-Toluene Solution

Amount of Sample Injected, µl	Attenuation	Peak Area			Average Area Attenuation = 400
		1	2	3	
0.6	400	86	88		87
0.7	400	95	98		97
0.8	400	111	117		114
0.9	800	68	64	64	131
1.0	800	75	74		149

Benzene = 0.9665%

Density of solution at 25°C ≃ Density of Toluene = 0.8623 g/ml[17]

Table 16. Calibration Curve, Toluene-n-Hexane Solution

Amount of Sample Injected, μl	Attenuation	Peak Area 1	2	3	Average Area Attenuation = 100
0.4	100	119	122	121	121
0.5	200	81	79		160
0.6	200	99	97		196
0.7	200	109	114		223
0.8	200	133	130	130	262
0.9	400	72	72	78	283
1.0	400	83	76	82	321

Toluene = 0.9003%

Density of solution at 25°C ≃ Density of n-Hexane = 0.6548 g/ml[17]

Table 17. Calibration Curve, Ethylbenzene-n-Hexane Solution

Amount of Sample Injected, μl	Attenuation	Peak Area 1	2	3	Average Area Attenuation = 64
0.1	64	68	70		69
0.2	64	131	140	130	134
0.3	128	95	94	99	192
0.4	128	127	136	132	264
0.5	256	80	85	84	332
0.6	256	97	101		396
0.7	256	114	115		460

Ethylbenzene = 0.7946%

Density of solution at 25°C ≃ Density of n-Hexane = 0.6548 g/ml[17]

Table 18. Calibration Curve, Isopropylbenzene-n-Hexane Solution

Amount of Sample Injected, μl	Attenuation	Peak Area 1	Peak Area 2	Peak Area 3	Average Area Attenuation = 32
0.3	16	92	86	89	45
0.4	32	57	59		58
0.5	32	74	69		72
0.6	32	88	89	86	88
0.7	32	107	101	110	106
0.8	64	60	59	61	120

Isopropylbenzene = 0.0746%

Density of solution at 25°C ≃ Density of n-Hexane = 0.6548 g/ml[17]

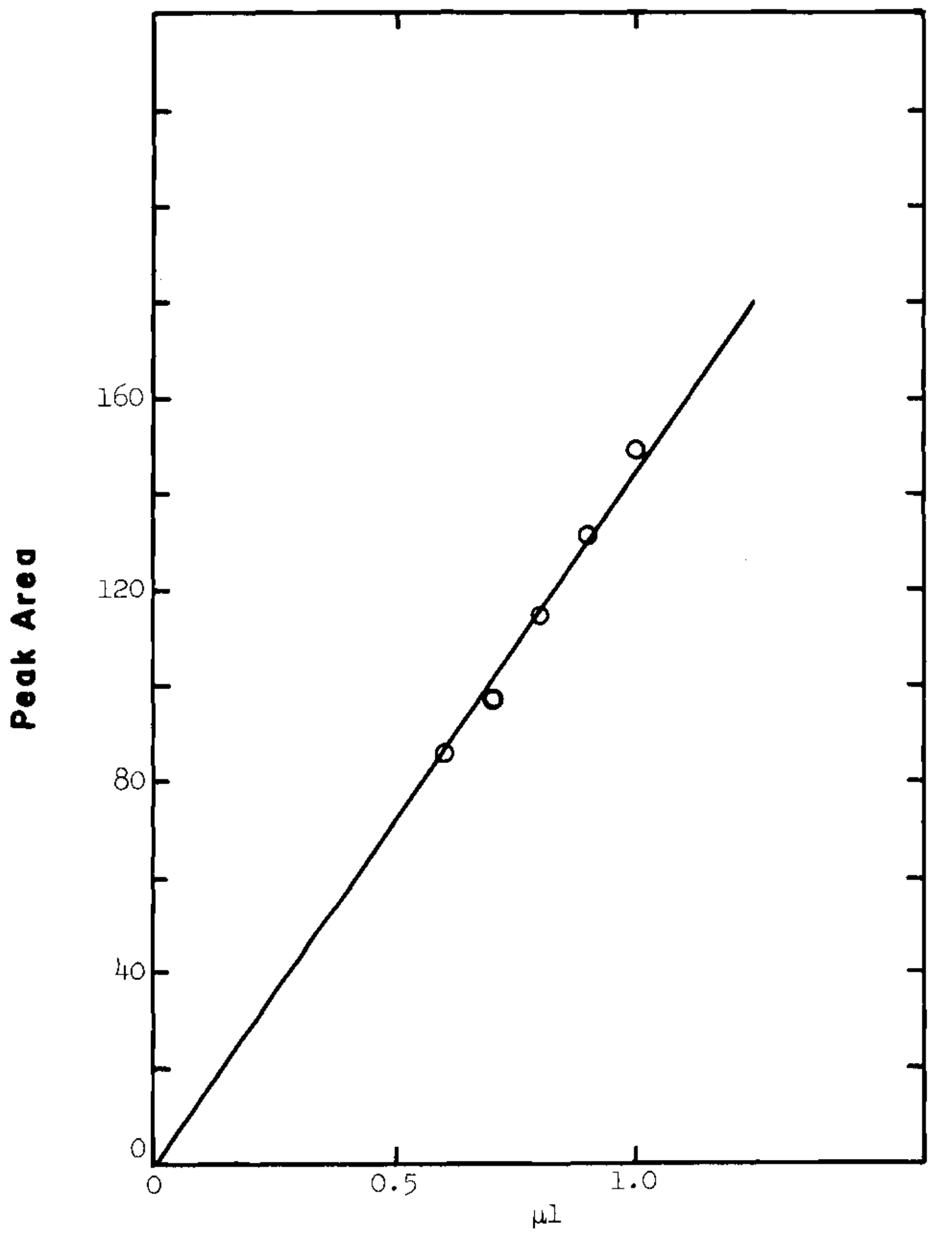

Figure 23. Calibration Curve, Benzene-Toluene Solution

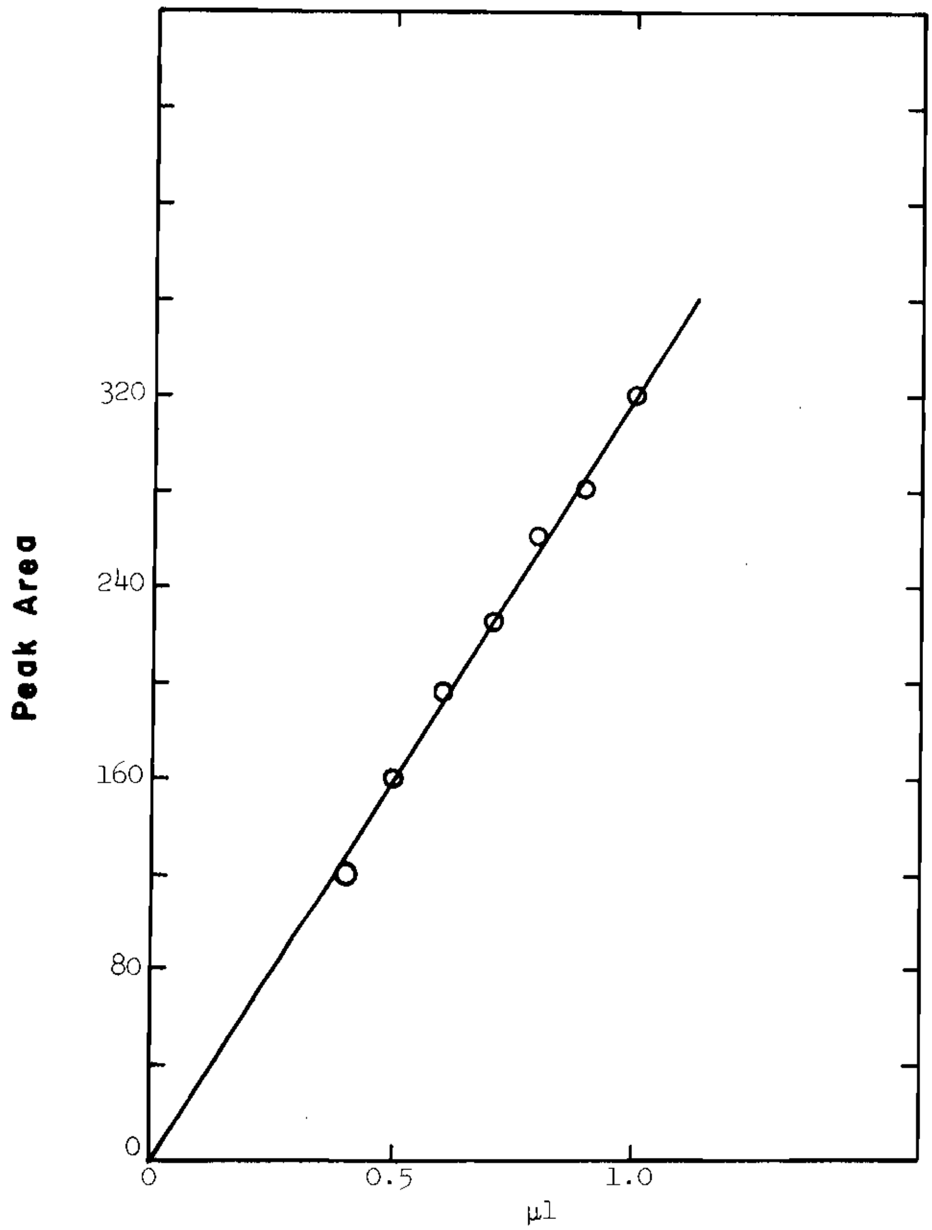

Figure 24. Calibration Curve, Toluene-n-Hexane Solution

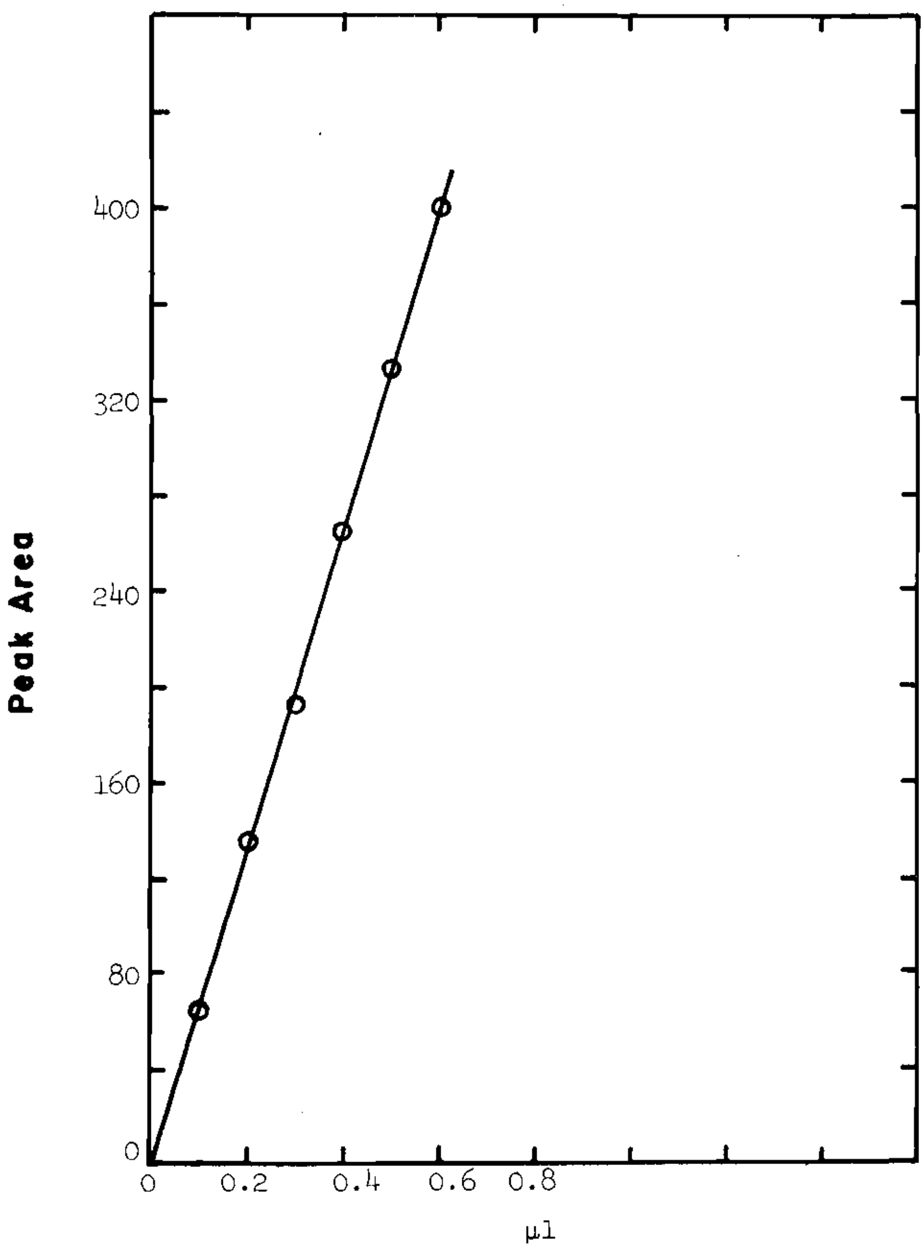

Figure 25. Calibration Curve, Ethylbenzene-n-Hexane Solution

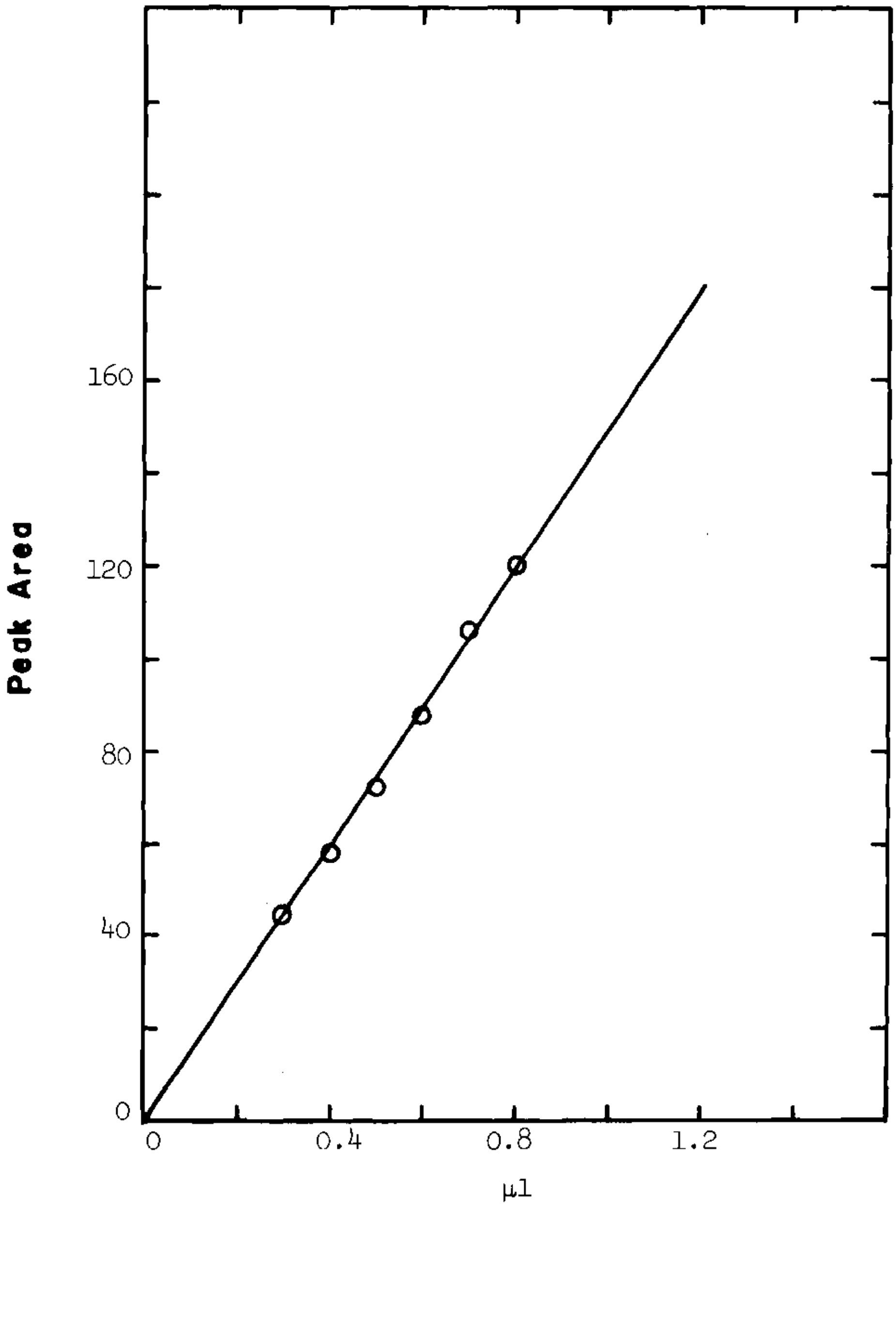

Figure 26. Calibration Curve, Isopropylbenzene-n-Hexane Solution

BIBLIOGRAPHY*

1. McAuliffe, C., J. Phys. Chem., 70, 1267 (1966).

2. Morrison, T. J., and Billett, F. J., J. Chem. Soc., 3819 (1952).

3. Franks, F., Gent, M., and Johnson, H. H., J. Chem. Soc., 2716 (1963).

4. Arnold, D. S., Plank, C. A., Erickson, E. E., and Pike, F. P., Chem. Eng. Data Ser., 3, 253 (1950).

5. Andrews, L. J., and Keefer, R. M., J. Am. Chem. Soc., 71, 3644 (1949).

6. Bohon, R. L., and Claussen, W. F., J. Am. Chem. Soc., 73, 1571 (1951).

7. McDevit, W. F., and Long, F. A., J. Am. Chem. Soc., 74, 1773 (1952).

8. Durand, R., Compt. Rend., 226, 409 (1948).

9. Fuhner, H., Chem. Ber., 57, 510 (1924).

10. Andrews, L. J., and Keefer, R. M., J. Am. Chem. Soc., 72, 5034 (1950).

11. Hoffmann, R. L., and Evans, C. D., Sci., 153, 172 (1966).

12. Kirshenbaum, I., Physical Properties and Analysis of Heavy Water, National Nuclear Energy Series, Manhattan Project Technical Section, Division III-Volume 4A, McGraw-Hill Book Co., 1951.

13. Steckel, F., and Szapiro, S., Trans. Faraday Soc., 59, 331 (1963).

14. American Petroleum Institute Research Project 14, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Page 362, (1954).

15. Kresheck, G. C., Schneider, H., and Scheraga, H. A., J. Phys. Chem., 69, 3132 (1965).

---

*The abbreviations used here follow the form used by Chemical Abstracts, 55, Part 9, p. 12J.

BIBLIOGRAPHY (Concluded)

16. Herington, E. F. G., J. Am. Chem. Soc., 73, 5883 (1951).

17. Timmerman, J., Physico-Chemical Constants of Pure Organic Compounds, Vol. II, Elsevier Publishing Co., New York, 1950.