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VAPOR-LIQUID EQUILIBRIA OF METHANOL-CARBON TETRACHLORIDE IN SOLUTIONS OF LOW METHANOL CONCENTRATION[*]

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Abstract

The vapor-liquid equilibria of solutions 0.0002 to 1.0 mole fraction methanol in carbon tetrachloride at 10, 20, 30, 40 and 50°C have been examined. The equilibrium vapor and liquid compositions and the total pressure above these solutions at the five temperatures are reported. The "pure" vapor pressures of methanol, P_a^* (a function calculated from the quotient P_x/N_a of partial pressure of methanol P_a and mole fractions of methanol in the liquid N_a), and the calculated values of the heat of vaporization of methanol both conclusively indicate that in solutions more dilute than 0.001 mole fraction methanol there still exists strong intermolecular attraction. This interaction is attributed to the existence of methanol dimers. A value of 7.6 to 11.2 kcal/mole is estimated for the dissociation of the dimer; this is the energy of the hydrogen bond if there is one hydrogen bond per dimer, and if there are two hydrogen bonds per dimer the energy of the bond is one-half this value.

T-191-1

Introduction

In this investigation the concentration and temperature dependence
of the vapor-liquid equilibria of dilute solutions of methanol in carbon
tetrachloride have been studied by means of a new method of vapor analysis[1].

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[1] K. M. Sancier, To be published.

The concentration limit in the dilute region has been extended to solutions
0.0002 mole fraction methanol where the effect of the dissociation of hy-
drogen bonds of dimers can be examined.

Scatchard, Wood and Mochel[2] examined the equilibria of this system

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[2] G. Scatchard, S. E. Wood, J. M. Mochel, J. Am. Chem. Soc. 68, 1960-1963
(1946)

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and have calculated the excess free energy, heat of mixing and entropy
of mixing of the solutions as a function of concentration. Their con-
centration range was limited to solutions no less dilute than 0.0169
mole fraction methanol. However, it is in solutions considerably more
dilute than this that the extent of interactions between alcohol molecules
due to hydrogen bonding begin to be reduced to small values. Indeed, it
has been shown that interactions (hydrogen bonding) still exists in solu-
tions less dilute than 0.01 mole fraction alcohol by spectra[3] and by heat
of mixing[4].

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[3] J. Errera, R. Gaspart and H. Sack, J. Chem. Phys. 8, 63-71 (1940)
[4] K. L. Wolf, Trans. Far. Soc., Sept., 1790-90 (1936)

In the present study the data have been measured so that the partial pressures of methanol and carbon tetrachloride can be calculated for solution 0.0002 to 1.0 mole fraction methanol at temperatures of 10, 20, 30, 40 and 50°C. From these data are calculated the "pure" vapor pressure P^* and the molar heat of vaporization ΔH of the methanol and carbon tetrachloride. The dilute range of methanol has received more attention because of the interest in the dissociation of all hydrogen bonds, and less data has been taken in the more concentrated range which has received consideration by other investigators[2].

Discussion of Method

In order to study the thermodynamic quantities listed above, that data must be obtained from which the partial pressures of the components in equilibrium with its solution of known composition at various temperatures can be calculated. The following measurements will be made on the closed system consisting of a solution and its vapor in equilibrium at several fixed temperatures: P the total pressure above the solution, n_a the mole fraction methanol in the vapor, and N_a the mole fraction of methanol in the solution. The partial pressure of methanol P_a is calculated from the product:

$$P_a = P\, N_a$$

The partial pressure of carbon tetrachloride P_b is calculated according to

$$P_b = P - P_a$$

The apparatus used for studying the system is shown in Fig. 1. Incorporated in this apparatus are means for providing the necessary temperature control for the solution in the 500 cc flask, a dual-function mercury column for measuring P and for sampling the vapor for analysis, and means to withdraw small samples of the solution and to vaporize it for analysis.

Samples of vapor and liquid phases are analyzed in a specially designed mercury manometer which has been described in detail elsewhere[1]. The principle of its operation is briefly as follows: Vapor samples are condensed above the mercury meniscus of the lower leg of the special thermostated closed-end manometer, the other leg of which faces a vacuum, and the volume occupied by the sample is fixed at a given small value. When the condensed vapor sample and manometer have reached thermal equilibrium, the pressure exerted by the condensed vapor (now existing in both liquid and vapor phases) is read from the manometer. The analysis of the vapor sample is determined by this pressure and by a calibration of the corresponding pressures of synthetic vapor samples of accurately known composition. In short, the method is one of substitution and capable of high sensitivity for systems in which the components have appreciably different vapor pressures.

The apparatus can be considered in three parts: the 500 cc sample flask immersed in the water bath B in which the sample mixture is allowed to come to thermal equilibrium; the manometer, enclosed in a temperature jacket through which water is circulated to prevent condensation of vapor on the Hg meniscus, serves the purpose of measuring total pressure above the liquid mixture and as a valve to permit removal of vapor samples; and finally the deaerator above the sample flask which is a means of introducing more of either component into the sample flask and deaerating them before admission into the lower flask. A metal valve is provided to govern flow of new liquid into the lower flask or liquid sample

from the flask to the analysis manometer. A metal-glass seal which is vacuum tight and of considerable flexibility is provided by saran tubing. The liquid contained in the sample flask could easily be removed through the tube extending from the descrator to the bottom of the sample flask. For temperature indication five Beckman thermometers are calibrated, one at each temperature: 10,000, 20,000, 30,000, 40,000 and 50,000°C, against a Bureau of Standards calibrated platinum resistance thermometer. In fact, the resistance thermometer is also in the bath and connected to a Mueller bridge and a 1-meter galvonometer of 0.1 microvolt per millimeter sensitivity to serve as a check on the thermometers and as an excellent visual aid in setting the temperature regulator. The inner diameter of the manometer of the sampling section is about 12 mm. The mercury in the manometer must be at the same temperature as the sample solution to prevent condensation of the vapors from the latter. The smaller diameter tubing leading from the sample flask up and then down in the temperature jacket to the bottom leg of the manometer is to prevent mercury from entering into the sample flask. A large coarse glass frit is provided on top of the manometer to prevent mercury from splashing into the rest of the system when vapor samples are withdrawn. Bath temperatures of 10° and 20° were provided with the aid of an ice chest containing cracked ice over a large copper coil through which bath water was circulated. By means of S5 and S6 which control the flow of water through the cooling coil or through the by-pass, the temperature of the water in bath B could be kept just below the desired temperature, with a small amount of added heat from the regulator to provide the difference. The temperature could be controlled to $\pm0.001^{\circ}$C at any of the five temperatures using a toluene regulator, thyratron relay, and vigorous agitation in an insulated 5-gallon jar.

The general procedure used to measure N_a, n_a and P is as follows:

1. Prepare a mixture of methanol and carbon tetrachloride of approximately known composition.

2. Introduce the mixture into the sample flask, deaerate by pumping, and bring to temperature equilibrium.

3. Measure $\underline{P}$ from the manometer using a cathetometer with a reproducibility of ±0.01 mm.

4. Withdraw a sample of liquid through S7 and transfer sample to the analysis manometer (through S4 and S1) where $\underline{N}_a$ is determined.

5. Withdraw a sample of vapor through the manometer and transfer through S2 and S1 to the analysis manometer where $\underline{n}_a$ is determined.

6. Repeat (3) and (5) for each of the five temperatures of bath B: $10,000°$, $20,000°$, $30,000°$, $40,000°$ and $50,000°$C.

7. Repeat (4) to determine the final solution concentration.

8. Steps (1) through (7) are repeated for different mixtures in the sample apparatus.

About one hour is allowed for the attainment of thermal equilibrium of the solution in the sample flask. A total of about ten hours is required to complete steps (1) through (7).

Materials. Both methanol and carbon tetrachloride were dried by refluxing for about 3 hours in the presence of calcium sulfate. A quantity of about 4 liters of each were fractionated and the center half of the distillate collected. The distillation range of each liquid was less than $0.1°$C when allowance was made for changes in barometric pressure during the process; these temperatures were $76.6°$C for carbon tetrachloride and $64.7°$ C for methanol. The vapor pressure of the carbon tetrachloride was measured at $50°$C and found to be 304.06 mm mercury at $0°$C, a value which is low compared to the reported literature[5] value of 317.1 mm. The pressure

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[5] Lange's Handbook of Chemistry, Third Edition

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of the methanol was 411.25 mm of mercury at $0^{\circ}C$, which is high compared to 406 mm reported in the literature. Sufficient quantities of these materials were purified initially for all runs including the calibration for analysis.

Treatment of Data

In Table I are tabulated the following data for 15 runs each at five temperatures: P, N_a and n_a. The calculated values P_a and P_a° are also tabulated. All pressures are reported in millimeters of mercury at $0^{\circ}C$.

It is apparent that the composition of the liquid phase N_a in the sample flask changed as vapor samples were withdrawn starting at 10° and ending at $50^{\circ}C$. The values of N_a were measured only at the extreme temperatures, and the intermediate values were interpolated from the knowledge of the amount and concentration of the vapor removed for analysis. For runs 1 and 2, where the limit of sensitivity of the method is approached, the values of n_a show no regular temperature dependence and here the average values were used to compute P_a. As we shall see, the validity of the conclusions to be deduced will not be affected by this approximation.

The last column in Table I is the "pure" pressure P_a° of methanol calculated according to

$$P_a / N_a = P_a^{\circ}$$

P_a° is the calculated vapor pressure that methanol might have when its partial pressure at the particular concentration and temperature is extrapolated to unit mole fraction methanol. This is tantamount to assuming

Table I

Equilibria Data on the Methanol-Carbon Tetrachloride System

(Subscript a refers to methanol)

Run	T(°C)	P	n_a	n_a	P_a	P_a°
1	10	56.31	.000219	.00048	.0276	125
	20	90.80	.000218	.00049	.0444	205
	30	141.75	.000217	.00063	.0694	320
	40	212.15	.000216	.00033	.106	480
	50	307.24	.000215	.00050	.150	700
				Av.=.00049		
2	10	56.69	.000245	.00076	.0386	160
	20	91.04	.000244	.00036	.0619	250
	30	142.22	.000243	.00120	.0967	400
	40	212.70	.000242	.00062	.145	600
	50	308.36	.000241	.00065	.210	870
				Av.=.00068		
3	10	56.72	.000318	.00162	.0926	290
	20	103.99	.000317	.00162	.171	540
	30	142.03	.000316	.00164	.233	740
	40	213.15	.000315	.00164	.349	1110
	50	309.17	.000314	.00164	.506	1610
4	10	56.85	.000353	.00220	.125	350
	20	91.43	.000352	.00217	.198	560
	30	142.38	.000351	.00163	.232	660
	40	213.02	.000350	.00170	.362	1030
	50	309.31	.000349	.00158	.489	1400
5	10	61.23	.00124	.0810	4.96	4000
	20	97.91	.00117	.0620	6.06	5200
	30	150.40	.00110	.0510	7.67	6870
	40	222.85	.00103	.0410	9.14	8870
	50	321.57	.00096	.0340	10.0	11400
6	10	77.40	.00525	.254	19.6	3740
	20	115.11	.00494	.212	24.4	4940
	30	173.08	.00463	.200	34.7	7500
	40	251.40	.00436	.177	44.4	10200
	50	354.72	.00411	.170	60.3	14700
7	10		.00644	.290	22.2	3450
	20	120.48	.00605	.231	27.9	4600
	30	178.25	.00545	.224	39.9	7300
	40	257.55	.00518	.205	52.7	10150
	50	360.60	.00489	.186	66.9	13700

Table I (Continued)

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Run	$T(°C)$	P	s_a	n_a	P_a	$P_a°$
8	10	84.15	.0143	.289	24.3	1700
	20	135.66	.0140	.290	39.3	2800
	30	209.85	.0138	.292	61.2	4400
	40	307.76	.0136	.294	90.5	6650
	50	433.24	.0134	.296	128.1	9550
9	10	86.74	.0190	.317	27.5	1450
	20	137.89	.0187	.313	43.1	2300
	30	213.87	.0184	.314	67.1	3650
	40	315.25	.0181	.312	98.4	5450
	50	443.56	.0178	.313	138.8	7800
10	10	91.83	.0610	.342	31.4	520
	20	151.90	.0605	.347	52.6	870
	30	242.18	.0600	.351	85.0	1420
	40	369.80	.0590	.356	131.6	2230
	50	541.27	.0585	.360	195.0	3340
11	10	95.23	.1223	.355	33.8	275
	20	157.87	.1221	.352	55.5	455
	30	254.21	.1219	.362	92.1	760
	40	390.60	.1216	.374	146.1	1200
	50	580.13	.1213	.374	217.5	1790
12	10	96.27	.3550	.393	37.8	107
	20	160.61	.3545	.370	59.4	170
	30	258.69	.3540	.383	99.0	280
	40	400.23	.3535	.399	159.5	450
	50	600.58	.3530	.405	243.5	690
13	10	96.24	.3835	.450	43.3	113
	20	160.83	.3828	.400	64.2	168
	30	260.43	.3821	.401	104.5	275
	40	404.03	.3814	.406	161.4	425
	50	607.07	.3807	.411	249.5	655
14	10	56.54	.9936	.985	55.6	56.0
	20	98.64	.9936	.984	97.0	97.6
	30	166.29	.9937	.983	163.5	165
	40	268.19	.9937	.982	263.5	265
	50	416.43	.9938	.981	409.0	410
15	10	55.60	1.000	1.000	55.60	55.60
	20	97.11			97.11	97.11
	30	163.80			163.80	163.80
	40	264.02			264.02	264.02
	50	411.25			411.25	411.25

that Raoult's law holds at the particular concentration and temperature and that it can be extended to pure methanol. Figure 2 shows the plot of log P_A° versus -log N_A for the five temperatures.

The variation of P_A° with temperature at constant composition can be used to calculate the molal heat of vaporization of methanol in these solutions. From Table I it is apparent that N_A varies within a run from one temperature to another due to removal of vapor for analysis. An expanded plot of Fig. 2 is therefore used to obtain values of P_A° at the five temperatures for constant values of N_A.

The logarithms of the P_A° values of a constant N_A are then plotted against the reciprocal absolute temperature, and the slope of this function read graphically leads to the calculation of the molal heat of vaporization of methanol. The values of ΔH for methanol thus calculated are plotted in Fig. 3 against -log N_A for the extreme temperatures 10° and $50^\circ C$. The scattering of the points corresponds to experimental errors, as well as those involved in the graphical interpolations and slope reading. For comparison the concentration dependence of ΔH for carbon tetrachloride at $30^\circ C$ is shown in Fig. 3 by the dashed line; the abscissa now refers to carbon tetrachloride.

Errors. The reliability of the calculated values of the heat of vaporization of methanol depends upon the concentration; it is estimated to be about $\pm$ 100 cal/mole for solutions 0.001 to 1.0 mole fraction methanol and about $\pm$ 1000 cal/mole for solutions more dilute than 0.0007 mole fraction methanol.

The experimental value of the total pressure above the solution in the/sample flask is subject to the error of a non-ideal vapor. The maximum deviation is 1 and 2 percent at 10° and $50^{\circ}C$, respectively, for carbon tetrachloride and smaller by a factor of 100 for methanol. Applying the correction for carbon tetrachloride to the partial pressures observed for methanol introduced a deviation not larger than 1 percent in the calculated value of the heat of vaporization of methanol.

In the extremely dilute solutions (Runs 1 and 2) the deviations in the experimental values of n_a are rather large and average values were used to calculate P_a. The corresponding error introduced thereby in P_a^* in no way can account for the vast decrease in the value of this function in solutions where $N_a < 0.001$. The influence of the error in n_a on ΔH_a in this range of concentration and the deviations observed are correspondingly larger.

Discussion

One of the striking observations to be made from the study of the vapor-liquid equilibria of the methanol-carbon tetrachloride system is the rapid change of the "pure" pressure, P_a^*, of methanol with change in concentration. This behavior is seen in Fig. 2 where P_a^* rises to a maximum at about 0.003 mole fraction methanol and then falls rapidly to low values in more dilute solutions. At the maximum value of P_a^* at $50^{\circ}C$ the vapor pressure of methanol would apparently be about 20 atmospheres if the alcohol could be concentrated to "pure" liquid with the fraction of hydrogen bonds remaining constant. Methanol in this state would probably correspond to a gas like ethane in which Van der Waals' forces are principally active (about 3.5 kcal/mole). The solubility of this "gas" in carbon tetrachloride would be such that Henry's law would be obeyed, that is, P_a^* would be constant in dilute solutions.

However, the value of P_a^* decreases in solutions more dilute than 0.003 mole fraction methanol indicating that molecular interaction is still appreciable. The most plausible interaction that might still exist is hydrogen bonding between two methanol molecules forming a dimer. A less probable alternative would be solvent-solute interaction; but this would certainly require less energy than is involved here.

There seems to be ample evidence for the existence of alcohol dimers in these dilute solutions. An infrared study[3] shows that there exist perturbed OH bonds, presumably due to hydrogen bonding between alcohol molecules, in solutions as dilute as 0.002 mole fraction ethanol in carbon tetrachloride. Wolf has concluded from orientational polarisation measurements that methanol dimers are principally present in solutions more dilute than 0.02 mole fraction methanol.

Wolf has also estimated from heat of mixing experiments that the association energy of two ethanol molecules to form a dimer is about 10 to 16 kcal/mole, values which are two or three times larger than the energy required to dissociate a single hydrogen bond of a larger polymer. A value for the dimer association energy which compares favorably with 10 to 16 kcal/mole is obtained from Fig. 3. If in solutions less concentrated than 0.001 mole fraction methanol the rise in the ΔH_a value is assumed due entirely to the dissociation of dimers to monomers, it is apparent that the energy involved at $10^\circ C$ is at least 3.8 kcal/mole (the difference between maximum and minimum values of ΔH_a at $N_a = 0.001$), and it may be as high as 5.6 kcal/mole assigning all energy above the Van der Waal's energy of 3.5 kcal/mole to hydrogen bonding. Since a

However, the value of P_a^s decreases in solutions more dilute than 0.003 mole fraction methanol indicating that molecular interaction is still appreciable. The most plausible interaction that might still exist is hydrogen bonding between two methanol molecules forming a dimer. A less probable alternative would be solvent-solute interaction; but this would certainly require less energy than is involved here.

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mole of dimers of the single-bridge form $OH ---- OH$ has half as many hydrogen bonds, the value of dissociation energy of the hydrogen bond is between 7.6 and 11.2 kcal/mole, the van der Waals' correction making the higher value more probable. However a mole of dimers of the double-bridge form $RO \overset{H----}{\underset{----H}{}} OR$ has as many hydrogen bonds, and the value of the dissociation energy of the hydrogen bond is then between 3.8 and 5.6 kcal/mole. It appears therefore that the double-bridge form of dimer predominates in these dilute solutions, unless the very much larger value for the dissociation energy of the hydrogen bond is accepted for the single-bridge form of dimer.

If the sudden rise in the ΔH_a value at $N_a = 0.001$ is attributed to solute-solvent interaction, the interaction would amount to 3.8 to 5.6 kcal/mole, values which seem excessive for a weak hydrogen bond such as may form between methanol and carbon tetrachloride.

This calculation of the energy involved in dissociating the dimer assumes that all the molecules are dimerized at about $N_a = 0.001$ and that only monomers exert a vapor pressure. In like manner the ΔH_a values in Fig. 3 when reduced by the van der Waals' energy give the energy necessary for the reaction:

$$(ROH)_x \rightleftharpoons (ROH)_{x-1} + ROH$$

But before a value can be computed for the bond being dissociated in the polymer existing at the given concentration, the fraction of the various polymers must be known. Perhaps the infrared study of the association bands will supply the necessary information.

In dilute solutions the sudden rise in the value of ΔH_a provides further evidence of the existence of the interaction deduced from the decrease in the value of P_a° in the same concentration range. For solutions more dilute than $N_a = 0.0005$ the values of ΔH_a scatter within a range bordered by the lines drawn for 10° and $50^\circ C$, however there is little doubt that ΔH_a is decreasing with dilution and temperature increase. This behavior is in harmony with the existence of hydrogen bonds, such as dimers, which are destroyed by dilution and temperature increase. It will be observed that the heat of vaporization, ΔH_b, for carbon tetrachloride shown in Fig. 3 by the dashed line exhibits no vast changes such as are found for methanol.

Fig. 1.   Apparatus for studying vapor-liquid equilibria
of solutions.
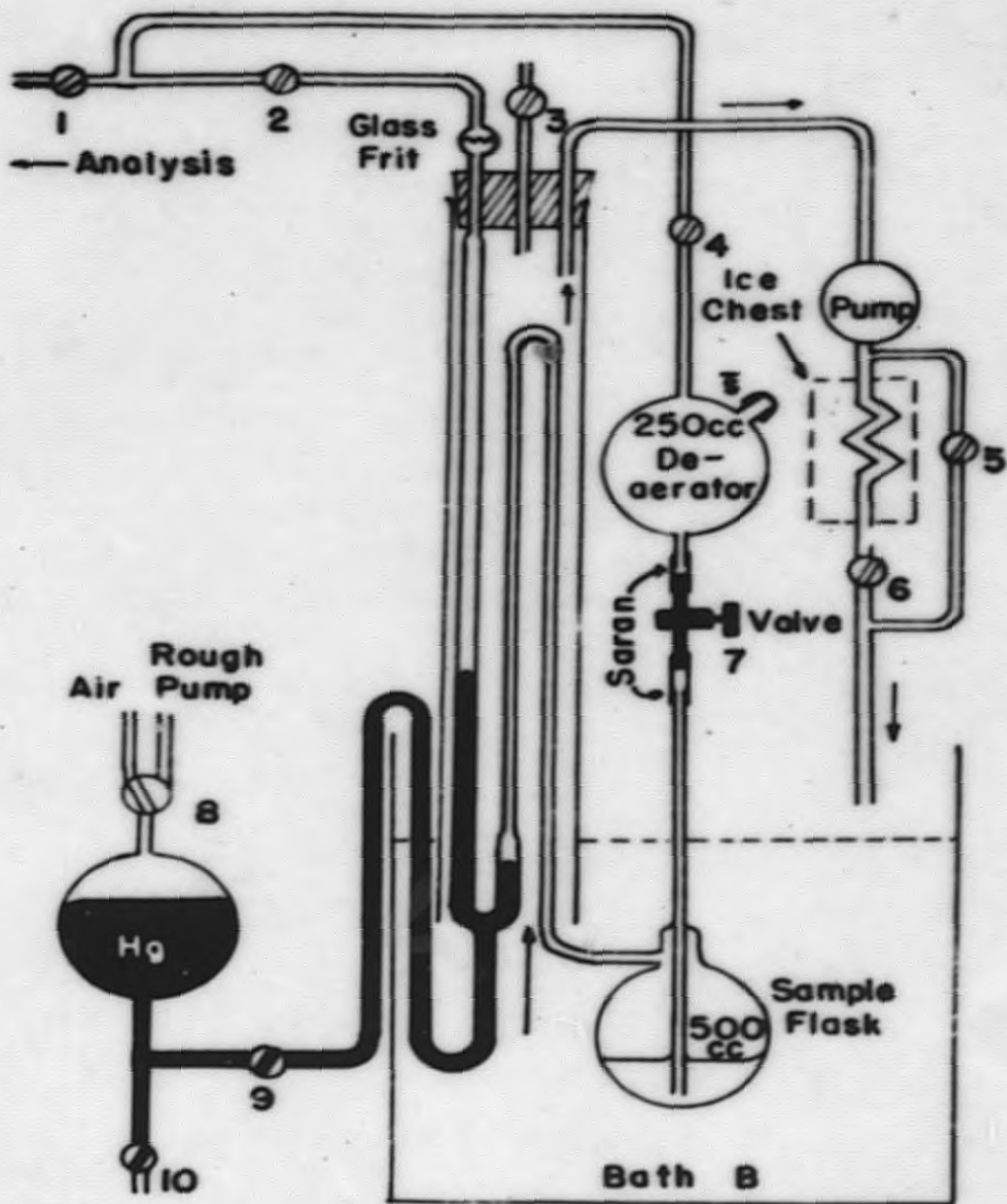
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Fig. 2. The "pure" vapor pressure P_A^o of methanol as a

function of its mole fraction N_A in carbon
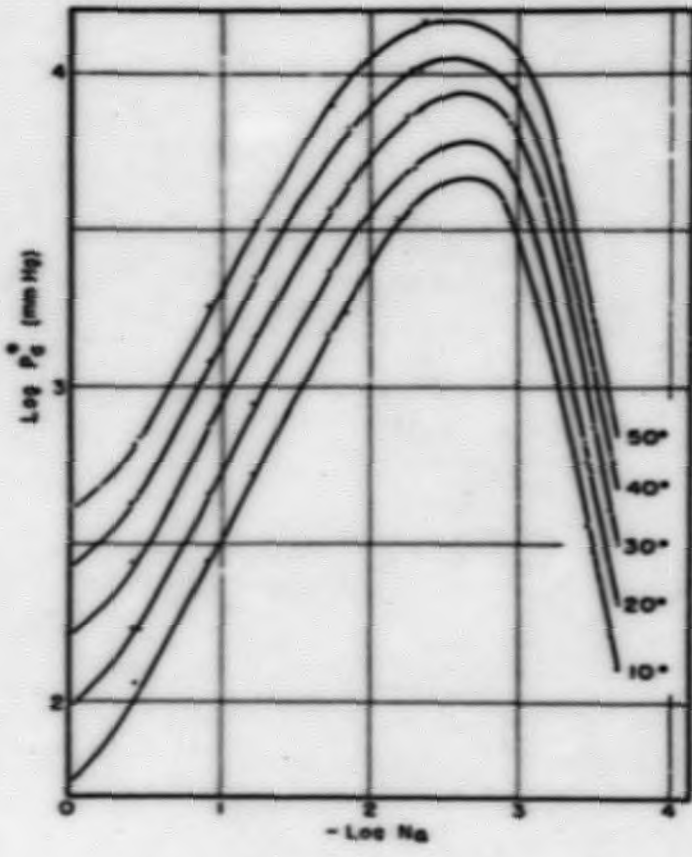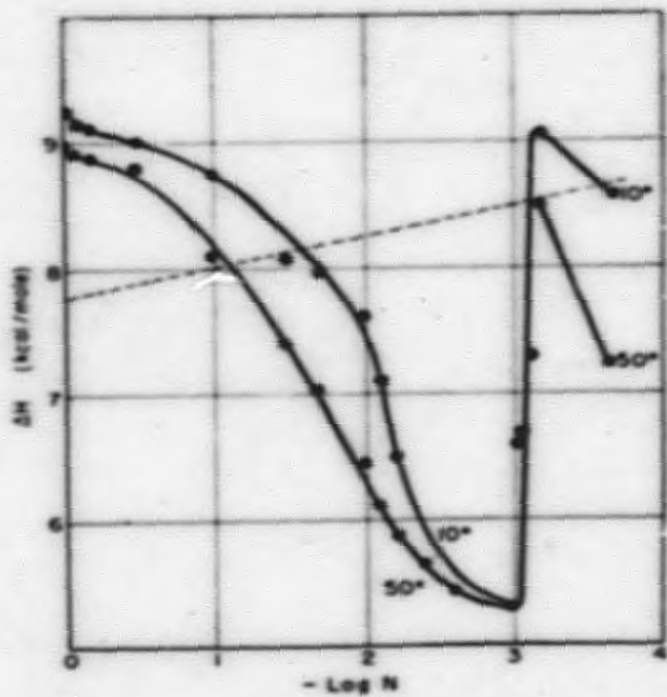
tetrachloride solutions at five temperatures.

Fig 2.

- Log Ng

Fig. 3. The heat of vaporisation ΔH of methanol (_____) at
10° and 50°C, and carbon tetrachloride (- - - -) at
30°C as a function of their respective mole fractions N.

Fig 3

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