for these measurements was estimated to be ±0.0002 g/ml. The densities of a given solution were found to decrease linearly with increasing temperature.

Multiple linear regression analysis was employed to obtain the following mathematical relationship among the density, temperature, and concentration:

$$d = 1.0122 + 0.1220\,(\mathrm{CuCl_2}) + 0.1618 \times 10^{-1}\,(\mathrm{HCl}) - 0.5085 \times 10^{-3}\,(t) - 0.2770 \times 10^{-2}\,(\mathrm{CuCl_2})\,(\mathrm{HCl}) - 0.1320 \times 10^{-3}\,(\mathrm{CuCl_2})(t)$$

where

d = density, g/ml
t = temperature, °C
(HCl) = molar concentration of HCl
($CuCl_2$) = molar concentration of $CuCl_2$

The standard deviation of the equation is ±0.0011.

Table II summarizes viscosities of copper(II) chloride solutions at different temperatures. A linear relationship was observed between the reciprocal of the absolute temperature and the logarithm of the viscosity of a solution of given composition. The experimental error for the least precise data was estimated to be ±0.003 cP.

The following equation can be used to calculate viscosities for copper(II) chloride solutions in hydrochloric acid.

Table II. Viscosities of Copper(II) Chloride Solutions in Hydrochloric Acid

Concn of $CuCl_2$, *M*	Concn of HCl, *M*	Viscosity, cP 30°C	50°C	70°C	90°C
1.496	7.08	1.693	1.189	0.884	0.667
1.524	6.00	1.621	1.122	0.823	0.633
1.492	5.06	1.552	1.076	0.779	0.604
1.500	4.08	1.496	1.028	0.742	0.570
0.992	4.94	1.369	0.966	0.707	0.548
0.502	5.00	1.208	0.865	0.646	0.506

$$\log_{10} \eta = [740.08 + 39.907\,(\mathrm{CuCl_2}) - 9.1775\,(\mathrm{HCl})]\frac{1}{T} + 0.05835\,(\mathrm{HCl}) - 0.006224\,(\mathrm{HCl})(\mathrm{CuCl_2}) - 2.54564$$

η = viscosity, cP
T = absolute temperature, K
(HCl) = molar concentration of HCl
($CuCl_2$) = molar concentration of $CuCl_2$

The standard deviation for this equation is ±0.010.

The vapor pressure data for the solutions studied are presented in Figures 1–4. A linear relationship between the reciprocal of the absolute temperature and the vapor pressures of HCl and H_2O was observed for the temperature range studied. The accuracy of the data reported is 10% for vapor pressures above 10 mm Hg and 15% for smaller vapor pressure data.

Although some efforts were undertaken to obtain a mathematical relationship for the vapor pressures as a function of temperature and concentration of HCl and H_2O, none of the equations obtained by multiple linear regression analysis were acceptable. The main obstacles to a suitable equation seemed to be the complex formation of $CuCl_2$ in hydrochloric acid and, to a certain degree, the limited amount of data.

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Physical Properties in Reaction of Ethylene and Hydrogen Chloride in Liquid Media

Diffusivities and Solubilities

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Determinations of diffusion coefficients and solubilities of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride were made to enable a detailed analysis of the kinetics of the ethylation of hydrogen chloride to ethyl chloride in the two liquid media (nitrobenzene and ethylene dichloride). The solubility of ethyl chloride in nitrobenzene was also determined. With nitrobenzene as the solvent, the solubilities of hydrogen chloride and ethylene were also determined at various concentrations of aluminium chloride, which was used as the catalyst in the ethylation reaction.

DIFFUSIVITIES

Experimental. Several methods (and apparatus) for determining diffusivities have been reviewed by Himmelblau (*4*). In the present work, a modified version of the Ringbom's apparatus (*12*) was used (Figure 1). It consisted of two capillaries fused together and connected to two different reservoirs through three-way capillary stopcocks. The fine capillary was 40 cm and the other 10 cm in length. The area of cross section of the fine capillary was 1.42×10^{-2} cm² and that of the other 3.413×10^{-2} cm². The reservoir flasks were of 250-ml capacity each. The side arm of the left reservoir was connected to a Hg manometer, the other end of which was closed. The fine capillary was graduated in mm and was calibrated before fusing. One more capillary cell with fine and coarse capillary cross sections of 1.25×10^{-2} and 6.876×10^{-2} cm², respectively, was fabricated.

Nitrobenzene, ethylene dichloride, ethylene, and hydrogen chloride of purity more than 99% were used. The purity was tested in a gas chromatographic apparatus.

The procedure adopted was similar to that of Smith et al.

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The diffusivities and solubilities of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride were determined at different temperatures. The solubilities of ethyl chloride in nitrobenzene and hydrogen chloride in nitrobenzene (containing aluminium chloride) were also determined. Three different empirical equations were used to correlate the data. The recommended equation is of the form

$$\ln X = a + b \ln T$$

where X represents either the diffusivity or solubility, T is the temperature in degrees K, and a and b are constants.

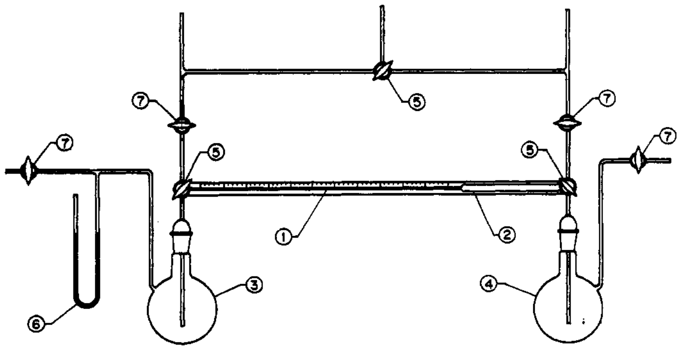

Figure 1 Apparatus for determining diffusion coefficients of gases in liquids

1. Fine capillary
2. Coarse capillary
3. Reservoir for gas-saturated liquid
4. Reservoir for pure liquid (gas free)
5. Three-way stopcock
6. Hg manometer
7. One-way stopcock

(*14*). In between gas-saturated and gas-free solvent columns, a pure gas phase was maintained. The gas-free solvent column was a dead-end column, whereas the gas-saturated solvent column was left confluent with the reservoir. As the gas diffused into the pure solvent, the gas-saturated column moved (replacing the gas diffused) toward the pure solvent column. This displacement was measured as a function of time. The system was fully closed to prevent any effect of atmospheric fluctuations. During a run the thermostat maintained constant temperature to ±0.05°C.

For analysis, the displacement, d, of the free meniscus in cm was plotted as a function of $t^{1/2}$ and by taking points beyond the initial equilibrium, we were able to determine the slope by the method of least squares. In the initial part of the experiment, when the absorption rate is high, the interface conditions are uncertain and so the observations had to be made for a longer period.

The values of the diffusion coefficients were calculated from the following equation of Stefan (*15*):

$$D = \frac{\pi}{4\,A^2Q^2}\left(\frac{V}{t^{1/2}}\right)^2 \tag{1}$$

where

$$A = \alpha_T\left(\frac{T}{273}\right)\left(\frac{P}{760}\right) \tag{2}$$

Values of α, the Bunsen absorption coefficient, required for calculating the diffusion coefficients of known systems were obtained from the International Critical Tables (*5*); and those of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride were calculated from the solubility data.

Test of Apparatus. A few systems, viz. carbon dioxide–water, oxygen–water, chlorine–water, and hydrogen sulfide–water, for which experimental values of diffusion coefficients are known, were first studied to test the apparatus. The values obtained for these systems were in good agreement with those reported by different workers, as shown in Table I, thus establishing the suitability of the apparatus.

Experimental Data. Experimental diffusivities of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride were determined at various temperatures and the results are presented in Table II.

To ascertain the reproducibility of the results, one particular run was repeated five times (for the hydrogen chloride–nitrobenzene system at 30°C), and the values obtained were: 2.3×10^{-5}, 2.0×10^{-5}, 2.32×10^{-5}, 2.27×10^{-5}, 1.9×10^{-5}, the average deviation from the mean value of 2.16×10^{-5} was 7.6%.

The values obtained for the hydrogen chloride–nitrobenzene and hydrogen chloride–ethylene dichloride systems are in good

Table I. Experimental Values of D for Known Systems (Test of Apparatus)

System	Temp, K	Exptl values obtained, $D \times 10^5$	Exptl value reported, $D \times 10^5$	Reference
CO_2–water	300.0	2.15	. . .	. . .
	298.0	. . .	1.90	(*20*)
		. . .	1.87	(*13*)
	303.0	. . .	2.29	(*11*)
			2.25	(*2*)
			2.15	(*17*)
Cl_2–water	303.0	1.59	1.62	(*10*)
			1.74	(*11*)
	298.0	. . .	1.89	(*2*)
O_2–water	303.0	2.90	. . .	. . .
	298.0	. . .	2.60	(*8*)
			2.42	(*2*)
H_2S–water	303.0	1.92	. . .	. . .
	289.0	. . .	1.77	(*3*)
	298.0	. . .	1.36	(*7*)

Table II. Experimental Values of Diffusion Coefficients

System	Temp, K	Exptl value of $D \times 10^5$
Ethylene–nitrobenzene	303.0	2.37
	313.0	2.71
	323.0	3.05
	333.0	3.29
Ethylene–ethylene dichloride	288.0	2.75
	292.0	3.35
	298.0	3.84
	303.0	4.11
Hydrogen chloride–nitrobenzene	299.0	1.75
	303.0	2.15
	313.0	2.38
	323.0	2.68
	331.5	2.92
Hydrogen chloride–ethylene dichloride	288.0	3.18
	298.5	3.89
	303.0	4.31

Table III. Values of Constants for Equation $\ln X = a + b \ln T$

System	Values of constants for diffusivity, $X = D$		Estimate of error in $\ln D$	Values of constants for solubility, $X = S$		Estimate of error in $\ln S$
	a	b		a	b	
Ethylene–nitrobenzene	-3.07×10	3.51	4.11×10^{-4}	3.67×10	-6.38	3.92×10^{-3}
Ethylene–ethylene dichloride	-5.39×10	7.68	2.99×10^{-3}	4.61×10	-7.96	4.67×10^{-3}
Hydrogen chloride–nitrobenzene	-3.62×10	4.44	4.19×10^{-3}	4.06×10	-6.60	7.76×10^{-5}
Hydrogen chloride–ethylene dichloride	-4.39×10	5.92	1.05×10^{-4}	4.54×10	-7.50	5.97×10^{-4}
Ethyl chloride–nitrobenzene	...	...	...	1.16×10^{2}	-1.92×10	5.03×10^{-3}
Ethyl chloride–ethylene dichloride	...	...	...	9.45×10	-1.54×10	1.40×10^{-1}

agreement (to within 10 and 5%, respectively) with the values predicted by the Wilke-Chang (*19*) equation, but for the ethylene–nitrobenzene and ethylene–ethylene dichloride systems the Wilke-Chang equation gives errors of 30 and 26%, respectively. Hence the Wilke-Chang equation is not recommended for predicting the diffusion coefficients for the latter systems.

Correlation of Data. To establish a relationship between diffusivity and temperature for each of the systems studied, the following empirical equations were used for fitting the data:

$$\ln X = a + \frac{b}{T} + c \ln T \quad (3)$$

$$\ln X = a + \frac{b}{T} + \frac{c}{T^2} \quad (4)$$

$$\ln X = a + b \ln T \quad (5)$$

where X represents the diffusivity, D, as in the present case, or the solubility, S as discussed in the subsequent section.

Since the values of error estimate in $\ln X$ for all the three equations are within the experimental error of 7.6%, it is evident that all the three equations fit the data well, and Equation 5 which is the simplest is recommended. The values of the constants and error estimate in $\ln X$ for Equation 5 are presented in Table III.

It may be noted from Figure 2 that, although good straight lines can be drawn for all the systems based on the Arrhenius form of temperature dependence, the existence of a weak but definite trend (as shown by the dotted curves) cannot be ignored. However, from Figure 2, approximate values of the activation energy (in cal/g-mol) for each system can be obtained: ethylene–nitrobenzene, 2288; ethylene–ethylene dichloride, 5072; hydrogen chloride–nitrobenzene, 2459; hydrogen chloride–ethylene dichloride, 4458.

SOLUBILITIES

Experimental. A glass vessel provided with a stainless steel stirrer and an outer jacket for circulating water at constant temperature (±0.05°C) was used. This kind of apparatus was chosen to obtain the solubility data under experimental conditions employed for the ethylation of hydrogen chloride to ethyl chloride (in nitrobenzene or ethylene dichloride as solvent).

Solvent, 400–500 ml, was introduced into the reactor, and the circulation of water at the required temperature was started through the outer jacket. After about 1 hr (when thermal equilibrium was reached), the gas was allowed to bubble through the liquid under constant stirring. Samples were withdrawn at intervals of 10–15 min for analysis, and this was continued until saturation was reached as indicated by constancy of at least 2–3 consecutive readings. Care was taken to ensure that no moisture entered the reactor, as this can greatly alter the solubility.

The same procedure was adopted for all the systems other than ethyl chloride in nitrobenzene. All the runs were carried out at a pressure of 0.93 atm (which is the atmospheric pressure at Poona). The barometric pressure was recorded for every run.

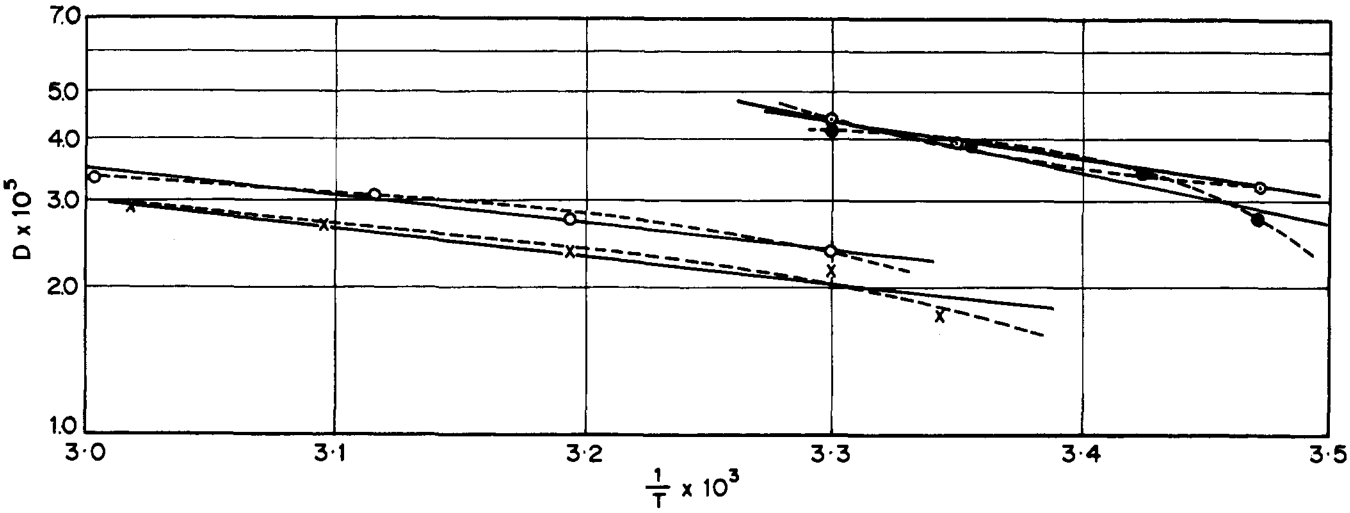

Figure 2. Temperature dependence of diffusion coefficient for systems studied

○ Ethylene–nitrobenzene
● Ethylene–ethylene dichloride
× Hydrogen chloride–nitrobenzene
⊙ Hydrogen chloride–ethylene dichloride

Analysis. Hydrogen chloride: 5–10 ml of a sample containing hydrogen chloride was introduced in a flask containing a known quantity of NaOH solution, the blank reading of which was already taken against standard HCl. Some NaOH was consumed by reacting with hydrogen chloride from the sample, and the excess NaOH was back-titrated against standard HCl. The difference between the blank and the back readings gave the amount of hydrogen chloride in the sample. The solubility of the HCl was then calculated from the relationship

$$S = \frac{(x_1 - x_2)\, N\, (36.5)}{x} \cdot 10^3 \qquad (6)$$

Hydrogen chloride in presence of aluminum chloride: Since aluminum chloride reacts with NaOH, the "blank" reading was taken by titrating with standard HCl, a sample of nitrobenzene containing aluminum chloride (but no HCl) which had been added to an aliquot of standardized NaOH.

Ethylene: Ethylene was analyzed by a method described by Thomas et al. *(18)* for the determination of olefins.

Ethyl chloride: The solubility of ethyl chloride in nitrobenzene was determined by a volumetric method, by desorbing the ethyl chloride in nitrobenzene at constant temperature (100°C). The solubility was plotted against $1/T$ and the line was extrapolated to obtain the solubility at 100°C. This value was added to the observed value to give the corrected value of the solubility.

Experimental Data. The solubilities of the systems ethylene–nitrobenzene, ethylene–ethylene dichloride, hydrogen chloride–nitrobenzene, hydrogen chloride–ethylene dichloride, and ethyl chloride–nitrobenzene were determined at different temperatures and at a pressure of 0.93 atm. The experimental error was found to be less than 2%, confirmed by 2–3 repetitions of a run. The results are presented in Table IV. For the system ethyl chloride–ethylene dichloride, the data reported by Stephen and Stephen *(16)* were used in working out the correlations.

The effect of aluminum chloride concentration on the solubility of hydrogen chloride in nitrobenzene is shown in Figure 3. The solubility is a mild function of aluminum chloride concentration (in nitrobenzene) at lower temperatures, and the greatest increase observed is of the order of 9.6% at 29°C in the concentration range studied. At higher temperatures, the effect of aluminum chloride is negligible.

Table IV. Experimental Values of Solubilities

(At 0.93 atm pressure)

System	Temp, K	Solubility in g/lit
Ethylene–nitrobenzene	286.0	1.97
	303.0	1.26
	313.0	0.99
	323.0	0.84
	333.0	0.76
Ethylene–ethylene dichloride	280.0	3.67
	287.0	2.66
	292.5	2.43
	300.5	2.05
Hydrogen chloride–nitrobenzene	302.0	18.98
	307.0	17.02
	323.0	15.11
	323.0	12.04
	332.0	10.22
Hydrogen chloride–ethylene dichloride	278.0	23.15
	293.0	16.36
	298.0	14.28
	305.0	11.78
	314.0	9.30
Ethyl chloride–nitrobenzene	298.5	620.0
	303.0	401.0
	308.0	296.3
	313.5	227.3
	323.0	128.6

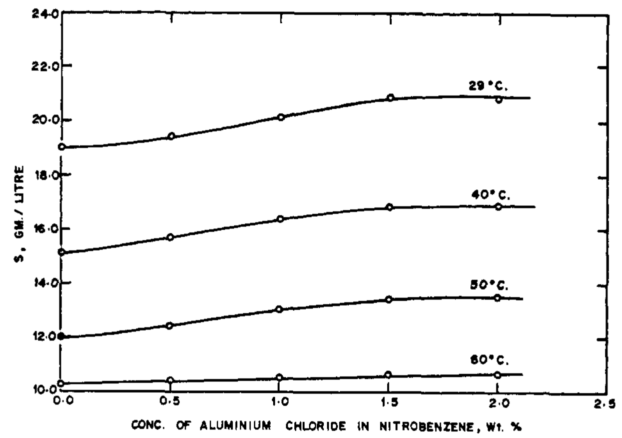

Figure 3. Solubility of hydrogen chloride in nitrobenzene in presence of aluminum chloride

Since ethylene formed a complex with the aluminum chloride and was also polymerized, an observation confirmed from reported data *(6, 9)*, no precise values of the solubility of ethylene in nitrobenzene containing aluminum chloride could be obtained.

Correlation of Data. As reviewed by Battino and Clever *(1)*, the types of equations normally used to fit the solubility data to establish the temperature dependence of solubility are the simple Arrhenius equation and an equation of the form represented by Equation 3. In the present case all the three forms used for diffusivity were tried (with S standing for X).

As discussed in the section on diffusivity, here also the values of the error estimate in $\ln X$ for all the three equations are within the experimental error of 2%, and the simplest form—i.e., Equation 5—is recommended for estimating the effect of temperature on the solubility. The values of the constants and the error estimate in $\ln X$ for Equation 5 are included in Table III.

From the Arrhenius plots (Figure 4), the approximate values of ΔH, the temperature-dependent heat of solution, can be obtained (as in the case of the activation energy of diffusion). The values of ΔH (in cal/g-mol) for the systems studied are: ethylene–nitrobenzene, 4898; ethylene–ethylene dichloride, 4767; hydrogen chloride–nitrobenzene, 4125; hydrogen chloride–ethylene dichloride 4651; ethyl chloride–nitrobenzene, 12040.

NOMENCLATURE

$$A = \alpha_T \left(\frac{T}{273}\right)\left(\frac{P}{760}\right)$$

a, b, c = arbitrary constants
D = diffusion coefficient, cm²/sec
E = activation energy for diffusion, cal/g-mol
N = normality of HCl
P = partial pressure of the gas under study, mm
Q = area of cross section of the absorbing interface, cm²
R = gas constant
S = solubility, g/lit
T = temperature, K
t = time, sec
V = volume of the gas displaced in time t, cm³
X = D or S
x = volume of the sample, cm³
x_1 = blank reading, cm³

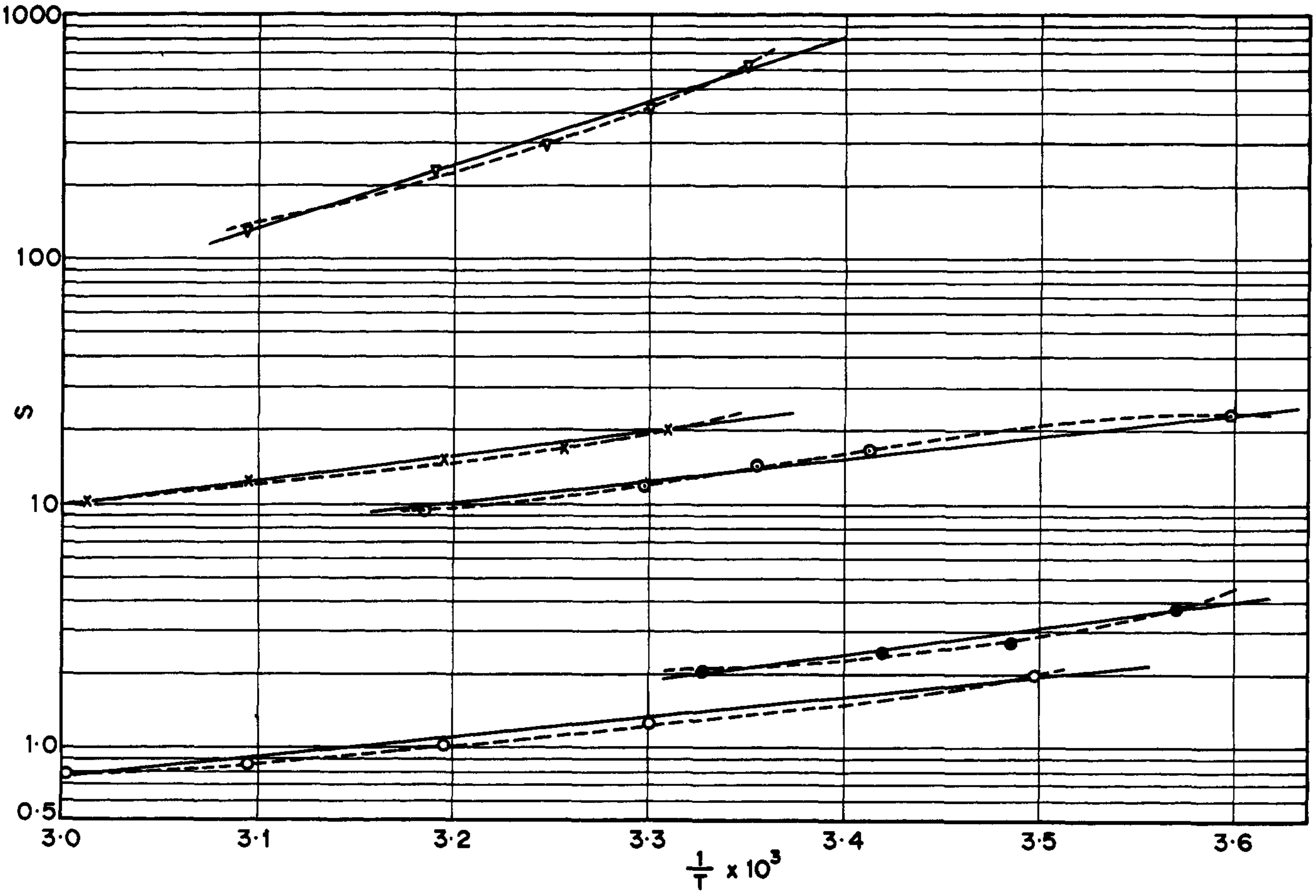

Figure 4. Temperature dependence of solubility for systems studied

○ Ethylene–nitrobenzene
● Ethylene–ethylene dichloride
× Hydrogen chloride–nitrobenzene
⊙ Hydrogen chloride–ethylene dichloride
△ Ethyl chloride–nitrobenzene

x_2 = back reading, cm^3
α_T = Bunsen absorption coefficient at the temperature T of the experiment
ΔH = temperature dependent heat of solution cal/g-mol

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