to prepare and maintain clean palladium–silver permeation tubes; $P^{1/2}$ dependence is present over a wide range of pressure; and the measured permeation rates, when compared with those of other investigators, are close to the highest observed under the same conditions.

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Specific Conductance of Concentrated Solutions of Magnesium Salts in Water-Ethanol System

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The equivalent conductances of dilute solutions of magnesium sulfate in water–ethanol solvents at 25°, 35°, and 45°C were presented in a previous paper. This work is an extension of that paper into the highly concentrated region. The specific conductance of concentrated solutions of magnesium sulfate were measured at 25°, 35°, and 45°C in pure water and in 20.1 and 40.7 wt % ethanol. An empirical equation is presented which fits the data well over the range of solvent compositions and temperatures studied. The empirical equation which relates the specific conductance at the maximum and the corresponding concentration at different solvent compositions and different temperatures is tested using the data presented here and that of Than and Amis for concentrated solutions of magnesium chloride in water–ethanol solvents at 25°, 35°, and 45°C.

Interest in the conductivity of concentrated solutions has increased greatly in the last few years; however, a satisfactory relationship between the specific conductance, L, and the concentration, C, has yet to be formulated which will work over a range of electrolytes, solvents, and temperatures. Than and Amis (5) presented an equation for magnesium chloride which gave good results over the range of concentrations, solvents, and temperatures studied. Their equation has the form of a modified normal distriution and is given by Equation 1.

$$L = L_m e^{-A(C-\mu)^2} \tag{1}$$

where

L = specific conductance
L_m = maximum specific conductance
C = concentration (moles/kg of solution)
μ = concentration corresponding to the maximum specific conductance
A = constant

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To test the significance of L_m and μ as important parameters in the conductance of concentrated solutions of electrolytes, the specific conductance of the bi-bivalent electrolyte, magnesium sulfate, was measured in the water–ethanol system at 25°, 35°, and 45°C. The equivalent conductances of dilute solutions of magnesium sulfate in water–ethanol solvents were reported in an earlier paper (2).

EXPERIMENTAL

All weights were previously standardized against NBS weights. The solutions were made up by weight corrected to vacuum using a Seederer and Kohlosbush 3-kg capacity balance with an average sensitivity of one division per 10 mg. The temperatures of the thermostated oil baths were held to ±0.01°C at 25°, 35°, and 45°C. Beckmann thermometers which had been previously standardized against and an NBS certified thermometer were used to read the bath temperatures. The densities of the mixed solvents were determined with a calibrated arm-pycnometer. The solvent compositions were

found in this manner within ±0.01 wt % ethanol. The dielectric constants of the solvents were interpolated from the data of Akerlof (1).

The resistances were measured with a Jones and Joseph 60,000-Ω bridge at a frequency of 1000 Hz. The resistances were precise within ±0.1 Ω with the smallest resistance measured being 613.2 Ω for magnesium sulfate in water at 45°C. It should be noted that the smallest resistance of magnesium chloride was 227.3 Ω based on the highest specific conductance of the water solvent at 45°C and a cell constant of 52.62 (5). It has been pointed out that in the ranges of 100 Ω, the Jones and Joseph bridge has an accuracy of ±1% (8). Due to the minimum resistances measured for both magnesium sulfate and magnesium chloride, the specific conductivity of the solutions should be accurate to at least 1% in the highly conducting solutions and considerably better than an accuracy of 1% for those solutions of greater resistance with a precision of ±0.1 Ω. NBS standard resistors of 1000.375 and 100.048 Ω gave bridge readings of 1000.4 and 100.0, respectively, at a room temperature of 23°C.

The Leeds and Northrup conductivity cell was calibrated using 0.1 and 0.01 demal solutions of purified fused potassium chloride with the values of the specific conductance given by Jones and Bradshaw (7). The cell constant was 51.912 and exhibited no tendency to change with the two standard solutions. The cell constant was also checked against two other cells of lower cell constants when measuring solutions of higher resistance. The cell constants of the cells used for intercomparison were 5.3886 and 1.0430 (2).

The conductivity water was prepared in the manner described by Foster and Amis (3) and consists of passing water, doubly distilled, over potassium permangate through a 1.5-m × 8-cm mixed bed ion exchange column. The specific conductance of the conductivity water ranged from 1-3 × 10⁻⁷ mho. Pure ethanol was prepared by the method of Smith (9). The general reaction is given by

$$RCOOC_2H_5 + C_2H_5ONa + H_2O \rightarrow RCOONa + 2C_2H_5OH$$
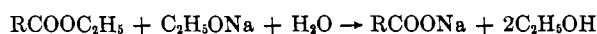
The reaction is carried out in the following manner: 28 grams of reagent grade sodium metal cut into small strips is added to 1 gal. of freshly opened reagent grade absolute ethanol. After the reaction is complete, 112 grams of ethyl phthalate is added, and the resulting solution is refluxed for 2 hr. The anhydrous ethanol is distilled slowly through a ³/₄-in. × 24-in. column packed with Raschig rings. The solvent is maintained under a dry atmosphere at all times and only the center cut of approximately 2 liters is used. The ethanol had a specific conductance of 4-7 × 10⁻⁸ mho.

Magnesium sulfate (reagent grade Baker's analyzed) was recrystallized from conductivity water three times and vacuum dried to the heptahydrate. The magnesium sulfate heptahydrate was converted to the anhydrous form by heating in a furnace at 650°C for at least 4 hr. The percentage of magnesium was determined by titration with EDTA and found to be 20.21 ± 0.01 compared to the calculated value of 20.20. The percentage of sulfate was determined by precipitation with barium chloride and was 79.78 ± 0.06 with the theoretical value being 79.80. The value of the ratio Mg/SO₄ was 1.001 ± 0.001.

The concentrated solutions of magnesium sulfate were prepared by adding a weighed amount of anhydrous magnesium sulfate to a quantity of solvent necessary for a stable saturated solution at a temperature slightly below 25°C. The concentration of each solution was checked both before and after dilution with a standard solution of EDTA using Eriochrome Black T as the indicator. In every case the results from the EDTA titrations agreed with the concentrations calculated by weight within the experimental error which was 1-2 ppt.

DISCUSSION

To find a more suitable equation for the specific conductance as a function of concentration, the following considerations should be taken into account: L must be zero at $C = 0$; L must be equal to L_m at μ; L must have a finite positive value at the saturation concentration (6). Equation 1 does not meet the requirement that $L = 0$ at $C = 0$ as can readily be seen.

Of the eight different nonlinear equations tried, the equation which gave the best fit to the data of magnesium sulfate has the form

$$L = C^a e^{bC^2} + cC + d \tag{2}$$

Table I. Constants Used in Equation 3 and Standard Deviations Obtained in Calculated Specific Conductances

Electrolyte	Solvent	Temp	μ	L_m	a	b	±Std. dev.
MgSO₄	00.0	25	1.4605	0.057943	0.63485	−0.28337	0.00022
		35	1.5098	0.071198	0.64371	−0.26057	0.00026
		45	1.5559	0.084625	0.65335	−0.24155	0.00029
	20.1	25	1.2519	0.016796	0.75542	−0.27719	0.00002
		35	1.2790	0.022055	0.76092	−0.26961	0.00003
		45	1.2987	0.027365	0.76740	−0.26548	0.00004
	40.7	25	0.36284	0.0022369	0.69623	−4.1308	0.000004
		35	0.38153	0.0029616	0.70342	−3.6751	0.000005
		45	0.36629	0.0035116	0.70160	−4.1741	0.000006
MgCl₂	00.0	25	2.0434	0.16033	0.67797	−0.14941	0.0020
		35	2.0758	0.19364	0.73814	−0.12557	0.0024
		45	2.1277	0.23155	0.69407	−0.13046	0.0027
	20.3	25	1.8064	0.069304	0.75472	−0.17999	0.0004
		35	1.8418	0.090025	0.75794	−0.16631	0.0005
		45	1.8657	0.11279	0.79314	−0.14959	0.0008
	39.8	25	1.5474	0.037857	0.61040	−0.27501	0.0001
		35	1.5739	0.049780	0.63462	−0.25162	0.0002
		45	1.6017	0.062919	0.65873	−0.22725	0.0002
	60.2	25	1.2631	0.021388	1.3363	0.0048175	0.0013
		35	1.3266	0.026866	1.3114	0.048114	0.0016
		45	1.3281	0.032975	1.1713	−0.040062	0.0013
	80.4	25	1.0148	0.0091648	0.66146	−0.42579	0.00002
		35	1.0442	0.011298	0.69921	−0.38270	0.00002
		45	1.0786	0.013616	0.72447	−0.34263	0.00002
	100	25	1.3616	0.022955	0.64209	−0.34271	0.0001
		35	1.7987	0.031880	0.70901	−0.17381	0.0000
		45	2.0331	0.042122	0.73996	−0.15685	0.0002

The equation was obtained in terms of L_m and μ by the following procedure: solve for the constant, e^d, in terms of L_m, μ, a, b, and c; take the first derivative with respect to C of the resulting equation and set it equal to zero, thus getting the constant c in terms of a, b, and μ. After substitution of the results for e^d and c into Equation 2, one obtains

$$L = L_m \left(\frac{C}{\mu}\right)^a e^{b(C - \mu)^2} - \frac{a}{\mu}(C - \mu) \tag{3}$$

The constants a and b were adjusted by weighting specific points on the experimental curve in order to make L_m and μ correspond to the experimental values when a maximum in the specific conductance actually occurred. When a maximum did not occur, the higher concentrations were given more weight and μ was calculated by taking the derivative of Equation 2 with respect to C and setting it equal to zero. Then L_m was evaluated from Equation 2 by substituting into it the value of μ. All of the calculations were carried out on an IBM 7040 computer, and the plots of the specific conductance vs. concentration were made with a Calcomp plotter (10, 11).

RESULTS

Table I contains the values of L_m, μ, a, and b for magnesium chloride and magnesium sulfate in various water–ethanol solvents and at three temperatures. Also listed is the standard deviation of the experimental values compared to those calculated by Equation 3. A sample of the agreement between observed and calculated results is shown in Table II. (Complete computer versions of Tables I and II have been placed with the American Chemical Society Microdepository Film Service.) The constants in Table I are based on the concentration in units of mol/kg so that the data may be compared to that of Than
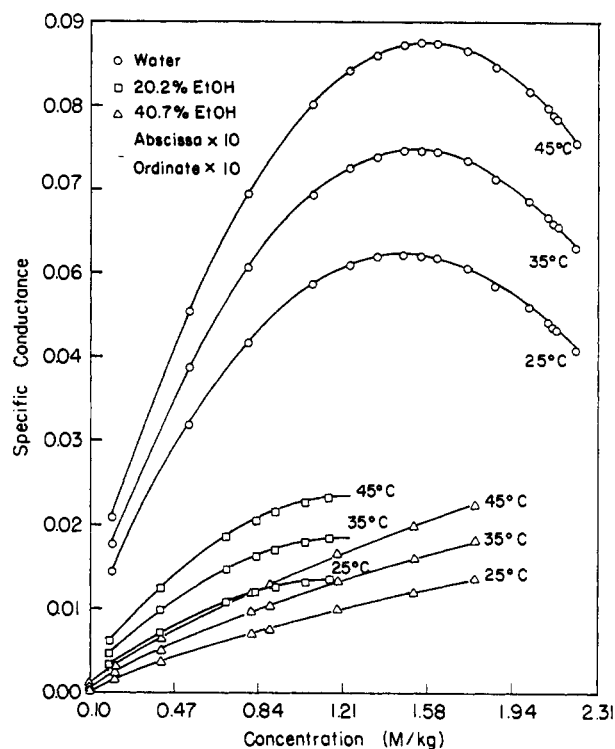

Figure 1. Specific conductance of magnesium sulfate in pure water, 20.1 and 40.7 wt % ethanol at 25°, 35°, and 45°C.
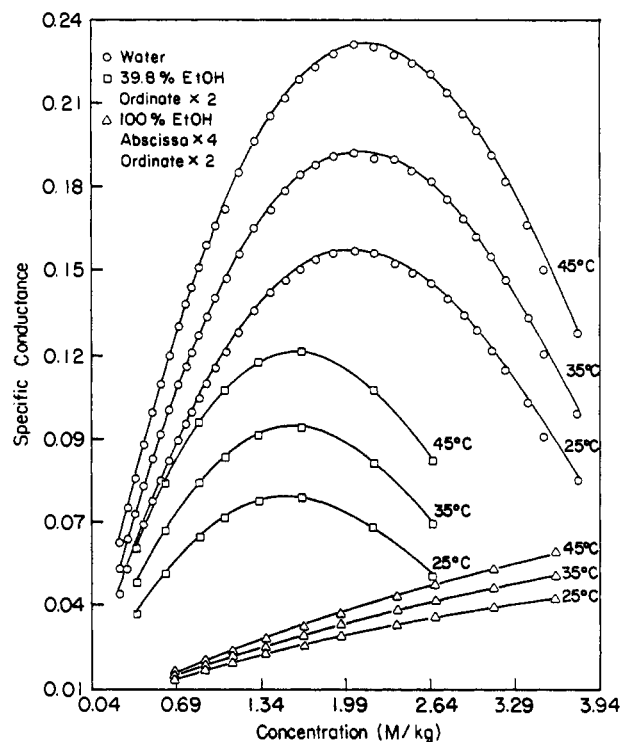

Figure 2. Specific conductance of magnesium chloride in pure water, 39.8 and 100 wt % ethanol at 25°, 35°, and 45°C

and Amis (5). Concentrations in mol/kg can be found by dividing moles/liter by the density of the solution. Figure 1 shows the plots of specific conductance of magnesium sulfate in water, 20.1 and 40.7 wt %. The experimental data are given by the points and the calculated values are represented by the solid line. Careful examination of the curves indicates that they are

Table II. Specific Conductance of Magnesium Sulfate in 20.1 wt % Ethanol at 25°, 35°, and 45°C

No.	Concn, m/l. × 1	Density, g/cc	Sp conduc × 1000	Calcd sp conduc × 1000	Ratio, C/μ	Ratio, $1./L_m$
			25°C			
1	1.265	1.1020	16.70	16.70	0.9168	0.9942
2	1.135	1.0891	16.39	16.40	0.8325	0.9761
3	0.9798	1.0759	15.71	15.71	0.7274	0.9356
4	0.8832	1.0654	15.09	15.11	0.6622	0.8987
5	0.7317	1.0490	13.88	13.85	0.5572	0.8264
6	0.4191	1.0138	9.90	9.93	0.3303	0.5895
7	0.1874	0.9881	5.62	5.61	0.1515	0.3346
	Standard deviation is 0.00002					
			35°C			
1	1.258	1.0963	21.86	21.86	0.8973	0.9912
2	1.129	1.0832	21.39	21.40	0.8149	0.9701
3	0.9742	1.0697	20.46	20.44	0.7120	0.9278
4	0.8784	1.0596	19.60	19.62	0.6481	0.8886
5	0.7279	1.0435	17.97	17.94	0.5453	0.8149
6	0.4170	1.0085	12.73	12.77	0.3233	0.5773
7	0.1864	0.9829	7.19	7.17	0.1483	0.3260
	Standard deviation is 0.00003					
			45°C			
1	1.251	1.0901	27.05	27.05	0.8837	0.9885
2	1.123	1.0775	26.41	26.43	0.8025	0.9652
3	0.9687	1.0637	25.21	25.18	0.7012	0.9213
4	0.8735	1.0537	24.11	24.14	0.6383	0.8812
5	0.7244	1.0385	22.05	22.01	0.5371	0.8058
6	0.4145	1.0027	15.52	15.58	0.3183	0.5672
7	0.1854	0.9774	8.72	8.69	0.1461	0.3188
	Standard deviation is 0.00004					

not entirely symmetrical and that the position of the maximum specific conductance seems to shift with increasing temperature.

Although the 20.1 wt % solvent did not give a maximum specific conductance before saturation occurred, the conductance at the higher concentrations indicated that if the curve could be extended, a maximum would have occurred slightly past the saturation point; therefore the calculated maximum for the 20.1 wt % solvent appears to be very good. The agreement between the experimental values and the calculated values of L_m and μ for the 40.7 wt % solvent may be questionable due to the large extension of the curve. However, it should be observed that they do occur at reasonable values.

Figure 2 shows the calculated and experimental values for magnesium chloride in water, 39.8, and 100 wt %. The agree-

ment between the calculated and experimental values is generally good except for the 60.2 wt % solvent which gave good agreement in the lower concentration range but includes poor results for the two highest concentrations. Close examination of the plots of magnesium chloride also show a tendency for the maximum specific conductance to shift with changing temperature.

The dependence of μ on temperature is presented in Figure 3 for magnesium sulfate and magnesium chloride for the various solvents. The plots are linear with increasing temperature with the exception of magnesium sulfate in 40.7 wt %. It was emphasized earlier that this solvent probably did not give accurate maxima for the specific conductance. Figure 4 is a plot of log L_m vs. wt % ethanol. The plot is reasonably linear
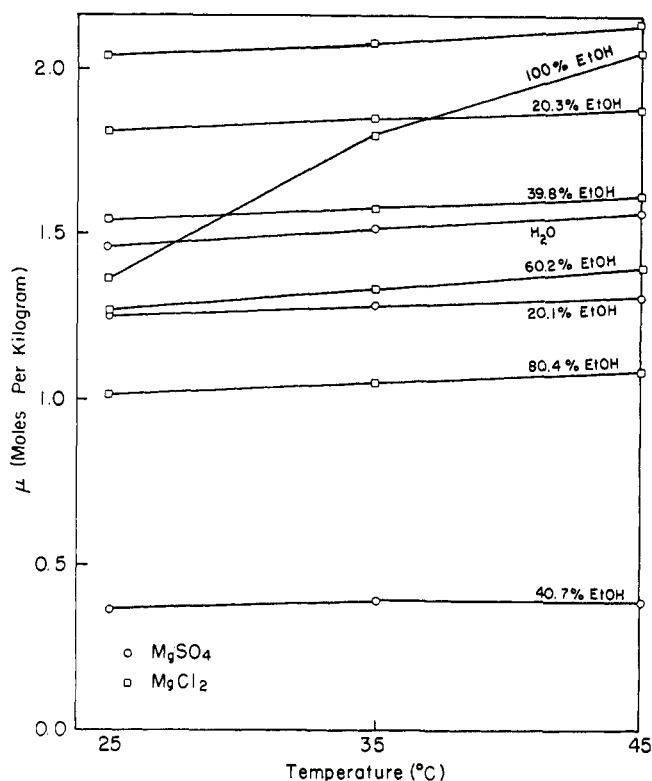

Figure 3. Plot of μ (mol/kg) vs. $T(°C)$ for MgSO$_4$ and MgCl$_2$ in various solvents
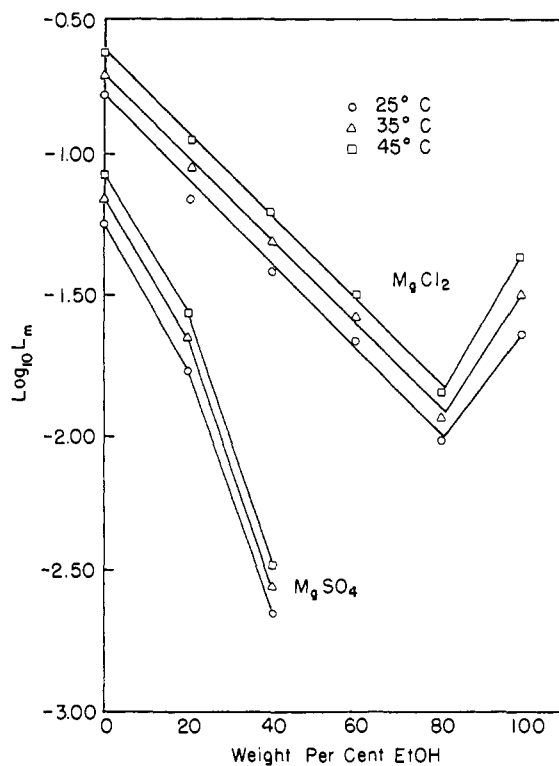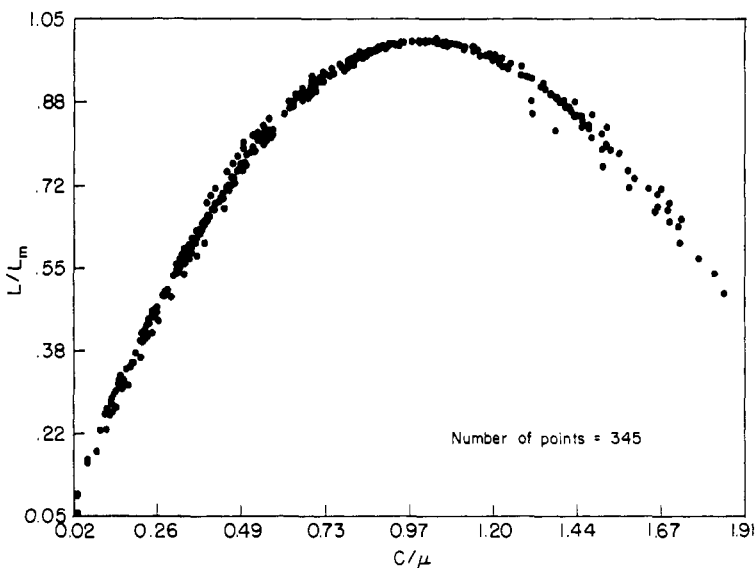

Figure 4. Plot of $\log_{10} L_m$ for MgSO$_4$ and MgCl$_2$ vs. weight percent EtOH

Figure 5. Plot of ratio of specific conductance to maximum specific conductance vs. ratio of concentration (mol/kg) to corresponding concentration for magnesium sulfate and magnesium chloride in water–ethanol solvents at 25°, 35°, and 45°C

for magnesium chloride except for the 100 wt % solvent. The marked decrease in the conductivity of magnesium sulfate is probably due to the decrease in solubility in higher weight percent solvents.

Inspection of the constants a and b show some of the following tendencies. The viscosity seems to influence the constant a in a reciprocal fashion since, in general, the constant a goes through a minimum at the middle weight percent solvents which is opposite in trend with the viscosity as a function of weight percent ethanol. The constant b tends to become more negative while the dielectric constant decreases, this may imply that there is a reciprocal relationship between b and the dielectric constant of the solvent as a function of temperature.

Figure 5 is an interesting graph of the ratio L/L_m vs. the ratio C/μ for the various solvents and temperatures of magnesium sulfate and magnesium chloride with a total of 345 points. This plot may indicate that the opposing forces acting on the electrolyte at the point on the conductance curve where $L = L_m$ and $C = \mu$ are virtually the same regardless of the temperature, solvent composition, and the nature of the electrolyte. The opposing effects are balanced at L_m and μ, thus giving two experimentally determined parameters which may be used in an empirical equation to represent the specific conductance of electrolytes in solvents that give maxima or for those solvents where the maxima may be found by a reasonable extension of the empirical equation.

In Equation 3, if theoretical significance could be assigned to constants a and b, the equation would become a theoretical one. The authors are working on this problem at present.

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Solubility of Propane and Carbon Dioxide in Heptane, Dodecane, and Hexadecane

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New data are reported for the solubilities of propane and carbon dioxide gases in normal heptane, dodecane, and hexadecane over the temperature range from 10–50°C.

The solubility devices used in these experiments were of the type described previously (5). The measurements entailed a small flow of deaerated solvent, continuously in contact with gas in a spiral tube, while the rate of gas absorption was measured volumetrically by observing the volumetric rate of shrinkage of gas confined at constant pressure in a buret over mercury. The mercury leveling bottle was raised by a rotating threaded shaft, chain-driven by a variable-speed motor of about 10–100 rpm. A spring-loaded half nut supporting the leveling table could be engaged into the rotating shaft at any desired elevation. The mechanical leveling device accurately controlled the gas volume and hence gas pressure. A U-tube in each of the solubility devices served to keep the volume of the absorbing system constant while solution was being accumulated. A difference in levels in the U-tube represented essentially the deviation in pressure from atmospheric pressure which could always be kept to less than 1 cm of liquid, and when the gas volume was read, to less than 0.1 cm, by suitable adjustment of the motor speed. The solubility measurements, therefore, were always performed at essentially atmospheric pressure.

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The design of the solubility apparatus permitted the measurement of the residual volume of vapor-free gas. In this design the problem of incomplete saturation of the gas with solvent vapor was entirely avoided. Care had to be taken, however, to maintain at least a small flow of gas from the gas buret into the absorption spiral at all times during the experiment to prevent any diffusion of solvent vapor back into the gas buret.

Two different solubility devices were used, one for high solubility (propane) and the other for moderate solubility (carbon dioxide) as shown in Figure 1. The first used a solution microburet and gas buret, of 5.0 ml (graduated to 0.01 ml), and 50-ml capacity, respectively. Deaerated liquid was charged into the apparatus by means of a Harvard Apparatus syringe pump using a 0.25-rpm motor along with a 10-ml gas-tight Hamilton syringe. The solvent infusion rate was 0.04402 ml per min. The volumetric infusion rate was determined accurately by weighing the quantity of distilled water delivered in a given period of time. The very low infusion rate for deaerated solvent was consistent with the very high propane solubility. The end of the syringe needle touched the wall of the spiral to ensure that an uninterrupted film of solvent flowed