Solubility of Chlorofluoromethanes in Nonvolatile Polar Organic Solvents

LYLE F. ALBRIGHT, PAUL T. SHANNON, FRANCOIS TERRIER, and PING LIN CHUEH

Purdue University, Lafayette, Indiana

Considerable solubility information has recently become available as a result of investigations to determine suitable chemicals for absorption refrigeration (*1, 6, 7, 8*). Solubility data were obtained for several chlorofluoromethanes in organic polar solvents from about 20° to 95°C. and from 0 to 100% solute concentrations. When dichloromonofluoromethane or chlorodifluoromethane was used, the solubility results generally indicated more solubility than that of an ideal solution. These high solubilities are caused by hydrogen bonds between the solute and solvent. Solubilities less than predicted by Raoult's law were apparently caused by preferential hydrogen bonding between solvent molecules. When a solute which contained no hydrogen atom, such as trichlorofluoromethane or trifluorobromomethane, and/or a nonpolar lubricating oil were used (*2, 3*), relatively low solubilities were obtained in all cases owing to a lack of hydrogen bonding between the solute and solvent.

Some of the solvents previously investigated contain more than one polar group, for example tetraethylene glycol dimethyl ether has five ether oxygen. Mastrangelo (*5*) proposed a method involving activity and activity coefficients of predicting the number of solute molecules that complex (or hydrogen bond) with each solvent molecule. This correlation requires solubility data at relatively low concentrations of solute in the solution.

In this investigation additional solubility data were obtained; these data plus previous data (*1, 6, 8*) were employed to test Mastrangelo's technique for several types of organic solvents. In addition a method for predicting the heats of mixing was shown to be quite reliable.

TABLE 1. SOLUBILITY OF DICHLOROMONOFLUOROMETHANE IN TRI EGDE AND CHLORODIFLUOROMETHANE IN DMA

	Triethylene glycol dimethyl ether (tri EGDE)		N, N-dimethylacetamide (DMA)	
Temperature, °C.	Pressure, lb./sq. in. abs.	Mole fraction $CHCl_2F$	Pressure, lb./sq. in. abs.	Mole fraction $CHClF_2$
20.0	2.2	0.378	9.3	0.260
	4.3	0.548	16.0	0.370
	9.1	0.697	27.3	0.496
	16.2	0.859	48.3	0.626
	—	—	73.6	0.735
35.0	2.42	0.259	15.8	0.259
	2.75	0.290	24.5	0.368
	3.8	0.377	42.9	0.494
	8.4	0.546	110.0	0.733
	15.4	0.696	—	—
	27.0	0.857		
50.0	4.27	0.259	24.2	0.257
	4.93	0.289	38.5	0.366
	6.8	0.376	64.7	0.492
	14.2	0.543	107.0	0.619
	24.5	0.695	157.5	0.730
	42.2	0.856	—	—
60.0	6.09	0.258	31.3	0.256
	6.99	0.288	50.3	0.365
	9.7	0.375	82.2	0.489
	19.3	0.539	134	0.616
	33.7	0.694	195	0.728
	55.8	0.855	—	—
70.1	8.44	0.257	39.9	0.255
	9.64	0.287	64.0	0.364
	13.4	0.374	103.0	0.487
	26.4	0.536	165	0.612
	44.9	0.693	237	0.725
	72.4	0.854	—	—
80.3	11.45	0.256	50.4	0.254
	13.06	0.286	79.3	0.362
	18.0	0.372	127	0.483
	35.1	0.533	199	0.608
	59.2	0.692	286	0.723
	92.3	0.852	—	—
90.5	15.00	0.254	62.3	0.253
	17.31	0.283	97.2	0.360
	24.0	0.370	154	0.481
	45.7	0.529	236	0.603
	74.2	0.691	—	—
100.8	19.42	0.251	76.2	0.252
	31.2	0.368	183	0.477
	58.2	0.524	275	0.602
	93.9	0.689	—	—

SOLUBILITY RESULTS

The solubility apparatus and operating procedure were essentially the same as previously reported (*1*). Solubility data obtained for dichlorofluoromethane in triethylene glycol dimethyl ether (Tri EGDE) and for chlorodifluor-

---

Francois Terrier is presently with Mines de Valleroy, Valleroy, Meurthe, and Moselle, France. Ping Lin Chueh is at Cheng Kung University, Tainan, Taiwan.

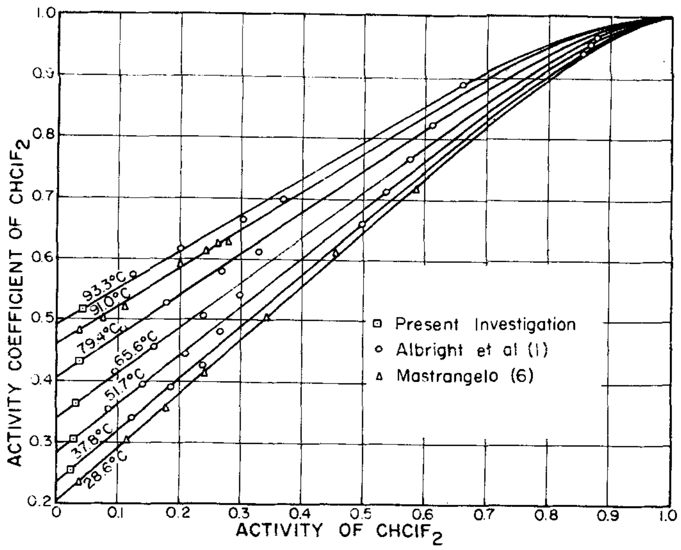

Fig. 1. Solubility correlation for system of tetraethylene glycol dimethyl ether and chlorodifluoromethane.

omethane in N,N-dimethylacetamide (DMA) are given in Table 1. Since the solvents had a low vapor pressure, the pressures at zero mole fraction solute are essentially zero. The data for each isotherm are represented in all cases by a smooth curve and indicate greater solubility than predicted by Raoult's law. In all cases cross plots of the pressure values vs. temperature at constant composition yielded smooth curves. Possible experimental errors were considered, and the pressure values are thought to be accurate to within about 1%.

The solubility information for chlorofluoromethanes in organic solutions which was presented earlier (*1, 6, 8*) was in many cases not extended to low solute concentrations. As a result additional measurements were made for seven binary systems, and the results are shown in Tables 2 and 3.

Limited solubility measurements were also made of chlorodifluoromethane in polydimethylsiloxane (50-centistoke viscosity). Extremely low solubility was found in the oil, and possibly immiscible liquid layers were present.

Two binary mixtures of solvents were also investigated (*7*). Diols, which are known to produce high positive deviations from Raoult's law (*1*), were mixed as follows with other compounds which give high negative deviations:

1. 16% (by wt.) 2,3-butanediol and 84% triethylene glycol dimethyl ether
2. 15% (by wt.) 1,4-butanediol and 85% triethylene glycol dimethyl ether.

The solubility results in each case indicated a decreased solubility of the dichloromonofluoromethane in the binary mixtures as compared with pure triethylene glycol dimethyl ether; however negative deviations from Raoult's law were obtained. Mixture (1) above resulted in slightly greater solubility than mixture (2). Although the solubilities in the pure butanediols were not measured, the results found here apparently lie close to a straight line interpolation of the results for the pure solvents; Thieme (*8*) made a similar observation for several other binary mixtures.

The results of the present investigation and those reported previously (*1, 6, 7, 8*) indicate the following order for the best solvents:

1. On a mole basis: tetraethylene glycol dimethyl ether (Tetra EGDE), triethylene glycol dimethyl ether (Tri EGDE), N,N-dimethylacetamide (DMA), and N,N-dimethylformamide (DMF).
2. On a weight basis the order is reversed since the molecular weights of the solvents vary significantly. The results for substituted amides are however essentially identical. The above comparison is applicable at all temperatures investigated.

FUNCTIONALITY OF SOLVENTS

Several solvents tested contain more than one polar group, and in theory at least hydrogen bonding could occur at each group. Steric hindrances or interaction of neighboring polar groups however prevent or minimize bonding at some polar groups. The specific interaction of the refrigerant type of solute *R* with a polar group of the solvent *S* at which hydrogen bonding occurs to form complex *RS* can be expressed as

$$R + S \rightleftharpoons RS \qquad (1)$$

Equation (1) forms the basis for the analysis of the experimental results. It

TABLE 2. SOLUBILITY OF DICHLOROMONOFLUOROMETHANE AND CHLORODIFLUOROMETHANE IN TETRA EGDE AND IN DMF

	Tetraethylene glycol dimethyl ether (tetra EGDE)				N, N-dimethylformamide (DMF)			
Temperature, °C.	Pressure, lb./sq. in. abs.	Mole fraction $CHCl_2F$	Pressure, lb./sq. in. abs.	Mole fraction $CHClF_2$	Pressure, lb./sq. in. abs.	Mole fraction $CHCl_2F$	Pressure, lb./sq. in. abs.	Mole fraction $CHClF_2$
37.8	1.27	0.158	4.02	0.0937	1.58	0.104	6.69	0.0776
	1.57	0.185	—	—	1.92	0.128	—	—
51.7	2.13	0.158	6.18	0.0921	2.65	0.104	9.53	0.0767
	2.60	0.184	—	—	3.20	0.127	—	—
65.6	3.47	0.157	9.04	0.0896	4.23	0.103	13.30	0.0756
	4.09	0.183	—	—	5.06	0.127	—	—
79.4	5.38	0.156	12.41	0.0862	6.51	0.103	18.00	0.0733
	6.29	0.182	—	—	7.78	0.126	—	—
93.3	7.95	0.154	16.23	0.0819	9.72	0.102	23.62	0.0705
	9.24	0.180	—	—	11.60	0.125	—	—
104.4	10.53	0.152	—	—	—	—	28.74	0.0674
107.2	12.84	0.177	20.20	0.0768	14.10	0.101	—	—
	—	—	—	—	16.71	0.124	—	—

TABLE 3. SOLUBILITY OF DICHLOROMONOFLUOROMETHANE IN ETHYLLAURATE, DIETHYLOXALATE, AND DIETHYLADIPATE

	Ethyllaurate		Diethyloxalate		Diethyladipate	
Temperature, °C.	Pressure, lb./sq. in. abs.	Mole fraction $CHCl_2F$	Pressure, lb./sq. in. abs.	Mole fraction $CHCl_2F$	Pressure, lb./sq. in. abs.	Mole fraction $CHCl_2F$
37.8	4.18 8.60	0.232 0.405	3.40 —	0.180 —	3.60 —	0.239 —
51.7	6.33 13.1	0.231 0.402	5.26 —	0.179 —	5.56 —	0.238 —
65.6	9.28 19.2	0.229 0.397	7.87 —	0.178 —	8.34 —	0.237 —
79.4	13.01 27.0	0.226 0.390	11.37 —	0.177 —	12.05 —	0.235 —
93.3	17.73	0.221	15.77	0.175	16.93	0.232
107.2	23.20	0.215	21.36	0.172	22.53	0.227

is written under the assumption that only one type of complex is formed between refrigerant and solvent. Thus one attributes the nonideal behavior in the liquid as caused by the formation of a complex due to hydrogen bonding between solvent and solute. The equilibrium constant K for the interaction of Equation (1) expressed in terms of activities is

$$K = \frac{a_{RS}}{a_R a_S} \qquad (2)$$

Mastrangelo's (5) model, which regards the solvent as a number of energetically identical sites and equates the activities to the effective concentrations, gives the activity coefficient of the liquid solute in terms of the activity of the liquid solute as

$$\gamma_R = K_1 + K_2 a_R + (1 - K_1 - K_2) a_R^2 \qquad (3)$$

where

$$K_1 = \frac{1}{f(1 + K)} \qquad (4)$$

$$K_2 = 1 + \frac{K - 1}{f(1 - K)} \qquad (5)$$

K_1 and K_2 can be evaluated at a given temperature by plotting a_R vs. γ_R; the plot at lower activity values is essentially a straight line whose intercept is K_1, and the slope at $a_R = 0$ is K_2. The functionality f (number of active sites per molecule) and the equilibrium constant K then can be determined from Equations (4) and (5).

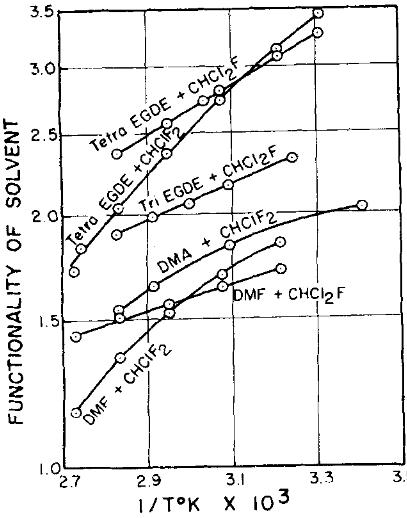

Fig. 2. Functionality of solvents in systems studied.

The calculation of γ_R and a_R from the experimental P-T-X data is done independently of any microscopic model proposed to explain the data. However the calculated γ_R and a_R serve to test the model so that their calculation indirectly affects conclusions about the validity of the model. Mastrangelo calculated γ_R and a_R from his data with the equations

$$a_R = \frac{p_{RG}}{p^\circ_{RG}} = \gamma_R x_R \qquad (6)$$

as this relation resulted simply in his statistical thermodynamic development of Equation (3) and his data were at relatively low pressure. Equation (6) assumes ideal gas behavior. However as shown in the Appendix[*] the γ_R and a_R values calculated from the equation

$$a_R = \frac{f_R^\circ}{f^\circ_{RG}} = \gamma_R x_R \qquad (7)$$

should be a function of the nonideal behavior of the liquid phase alone and thus provide an accurate check on the validity of the model.

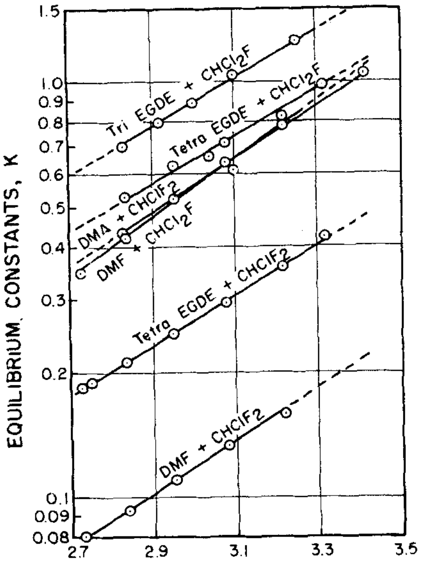

Fig. 3. Equilibrium constant for hydrogen bonding in various systems.

Solubility data of this investigation plus previous data (*1*, *6*, *8*) were tested by means of this refinement of Mastrangelo's approach as expressed by Equations (1), (2), (3), and (7). The fugacities of the pure liquid and vapor refrigerant were calculated on a Datatron-204 computer with the Beattie-Bridgeman or Martin-Hou equation of state (*4*). The specific volume of the liquid was taken as a function of temperature only in the calculation of the fugacity of the pure liquids.

The plots of a_R vs. γ_R for the mixture of chlorodifluoromethane and tetraethylene glycol dimethyl ether are shown in Figure 1 for temperatures from 28.6° to 93.3°C. The data for a given temperature are well represented by a straight line when a_R is less than about 0.4. Values of K_1 and K_2 as determined from Figure 1 are given in Table 4.[*] Similar plots were obtained for other systems, and the K_1 and K_2 values for these are also given in Table 4. In all cases γ_R values for a system increased with temperature.

Plots of a_R vs. γ_R (such as Figure 1) are sensitive to small inaccuracies of the solubility results. Such plots are then useful in testing the agreement between the results obtained here with those reported earlier. Previous results for tetraethylene glycol dimethyl ether (*1*, *6*) and for N,N-dimethylformamide (*8*) agree very well with the present data for these solvents. However the earlier data for the three esters (*1*) show poorer agreement with the present results. After a careful test to determine the reason for this disagreement it was concluded that the earlier data for esters are slightly inaccurate (equilibrium pressures of those results are probably too low by 1 to 2 lb./sq.in.).

The activity coefficient values calculated with Equation (7) show good

---

[*] Material has been deposited as document 7287 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C. and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

[*] See footnote in column 2.

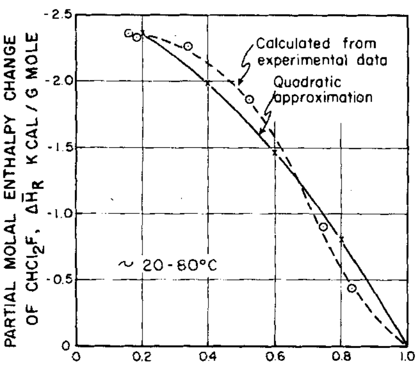

Fig. 4. Partial molal enthalpy change for chlorodifluoromethane in mixture with tetraethylene glycol dimethyl ether.

agreement with those values calculated from Equation (6) at low pressures (since the gases are essentially ideal). At higher pressures significantly different values were obtained. The calculated functionality values are also given in Table 4.* Figure 2 indicates the temperature dependence of these values for six of the systems studied. Although it is disappointing that a constant functionality value was not obtained for a given solvent at all temperatures studied as had been reported earlier (5), decreases in these values with temperature are not surprising. Probably steric hindrances increase with temperature. Mastrangelo (5) also suggests reasons for noninteger functionalities. Of considerable interest is the fact that functionality values of tetraethylene glycol dimethyl ether show similar temperature dependence for both dichloromonofluoromethane and chlorodifluoromethane (see Figure 2). Also the values for triethylene glycol dimethyl ether (with one fewer oxygen atom) are lower than the values for tetraethylene glycol dimethyl ether. The ratio of the functional oxygen atoms to the total oxygen atoms were found to be almost identical for both compounds.

Functionality values for the substituted amides also have almost identical temperature dependence (see Figure 2). Functionality values for systems with chlorodifluoromethane decrease somewhat more rapidly with temperature than values of those systems with dichloromonofluoromethane. However chlorodifluoromethane has a low critical temperature which is less than some of the temperatures investigated here.

The functionality values of esters also decrease with temperature. As was expected diethyl adipate has higher values than diethyl oxalate, which would presumably exhibit more steric hindrances to complexing. Diethyl oxalate (with two ester groups) has higher values than ethyl laurate (with one ester group). Apparently however the single-ester group of ethyl laurate is more effective than either one of the groups of diethyl oxalate or diethyl adipate. Equilibrium constants (K) of ethyl laurate are also higher than those of the more complicated esters.

N,N-disubstituted amides and ethyl laurate contain only one polar grouping, although each group contains two polar atoms. Since the functionalities of these compounds were found to be greater than one, apparently more than one solute molecule could complex with each group.

The fact that the functionalities of the molecules in this investigation were not integers or independent of temperature shows that the proposed model is only a good first approximation to the actual physical case. The model is still useful however as a sensitive procedure for checking experimental consistency and for interpolation. Further the use of average f and K values will give a good first approximation to the P-T-X behavior of these highly nonideal solutions.

HEAT OF HYDROGEN BONDING

Equilibrium constants for Equation (1) were calculated from the values of K_1 and K_2 and are given in Table 4.* The temperature dependence of the equilibrium constant is given by

$$\left[\frac{\partial \ln K}{\partial\left(\frac{1}{T}\right)}\right]_{p,x} = -\frac{\Delta H^\circ_R}{R} \qquad (8)$$

Figure 3 is the plot of the logarithm of K vs. the reciprocal of the absolute temperature for the ether and substituted-amide solvents. Relatively straight-line plots were obtained for each binary system; the slopes were all similar even though four solvents and two solutes were used in these systems. Values of K for the different systems varied rather appreciably at a given temperature; systems containing dichloromonofluoromethane have higher values than those systems with chlorodifluoromethane. Both K and ΔH°_R probably vary with the composition because of steric effects and interaction of neighboring complexes on the solvent molecule. Calculated values of K and ΔH°_R are however probably relatively accurate for low solute compositions. It is encouraging to note that for dichloromonofluoromethane in tetra EGDE the calculated value for $\Delta H^\circ_R = -2.63$k.cal./g. mole is in the range with values found in the literature.

Mastrangelo (5) used ΔH°_R (k.cal./g. mole of complex formed) to predict the overall heat of mixing, ΔH^M (k.cal./g. mole of solution). He has assumed that K and ΔH°_R are independent of the mixture composition and that the relationship between ΔH°_R and ΔH^M can be evaluated from the composition, K, and f. He obtained relatively good agreement with experimental heat of mixing data (9) for dichlorofluoromethane in tetraethylene glycol dimethyl ether at 3.5°C. Calculations to determine ΔH^M were repeated by means of the new values of ΔH°_R and K (obtained by extrapolation to 3.5°C.). ΔH^M values calculated in this manner were low by about 35%. It should be emphasized that small errors in the solubility data especially at low solute concentrations cause large differences in the calculated K values. Failure of this method for determining ΔH^M is not surprising since several of the assumptions made in the calculations are open to question.

HEAT OF MIXING

The heat of mixing may be calculated directly from the experimental data without any assumptions [that is Equation (1)] regarding the microscopic behavior of the system. The partial molal enthalpy change for the solute in a binary system is given by

$$\Delta\bar{H}_R = \left(\frac{\partial \Delta H_T^M}{\partial n_R}\right)_{T,p,n_S} = R\left[\frac{\partial \ln \gamma_R}{\partial\left(\frac{1}{T}\right)}\right]_{p,x_R} \qquad (9)$$

The following assumption is probably quite good:

$$\left(\frac{\partial \ln \gamma_R}{\partial(1/T)}\right)_{p,x_R} \cong \left(\frac{\partial \ln \gamma_R}{\partial(1/T)}\right)_{x_R} \qquad (10)$$

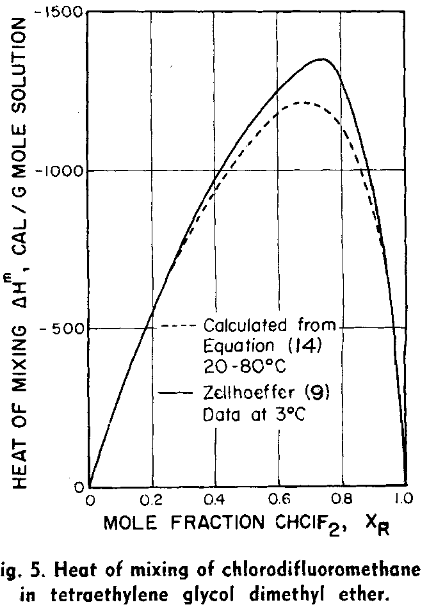

Fig. 5. Heat of mixing of chlorodifluoromethane in tetraethylene glycol dimethyl ether.

---

* See footnote on page 670.

* See footnote in column 1.

Plots were made of the logarithm of γ_R (activity coefficient of chlorofluoromethanes) vs. the reciprocal of absolute temperature at various compositions. The resulting curves were essentially straight lines in all cases, and the slopes were taken equal to the partial derivative. Figure 4 indicates the results found for $\Delta \overline{H}_R$ as a function of composition for the system of chlorodifluoromethane and tetraethylene glycol dimethyl ether.

In general $\Delta \overline{H}_R$ can be expressed fairly well by a quadratic function such as

$$\Delta \overline{H}_R = A + B\,x_R + C x_R^2 \qquad (11)$$

Since at $x_R = 1.0$ (pure R), $\Delta \overline{H}_R = 0$

$$\Delta \overline{H}_R = A(1 - x_R^2) + B(x_R - x_R^2) \qquad (12)$$

Substituting Equation (12) into Equation (9), integrating and noting that $\Delta H_T^M = 0$ at $n_R = 0$ one gets

$$\Delta H^M = \frac{\Delta H_T^M}{(n_R + n_S)} = -(2A + B)x_S \ln x_S - (A + B)x_R x_S \qquad (13)$$

The constants A and B were evaluated by the method of least squares to be -2.62 and 0.905 respectively for the system of chlorodifluoromethane and tetraethylene glycol dimethyl ether. Figure 4 indicates that the analytical expression gives a fair fit to the data. An expression for this system may be obtained by substituting A and B into Equation (13):

$$\Delta H^m = 4.33\, x_S \ln x_S + 1.71\, x_R x_S \qquad (14)$$

Figure 5 indicates the relatively good agreement between the calculated and the experimental values (9) at 3.5°C. Although several assumptions were made, the method seems reliable within about 10%. Improved agreement might be expected with a better equation than Equation (11) for fitting the $\Delta \overline{H}_R$ data. The accuracy of the present results probably does not justify such a refinement.

ACKNOWLEDGMENT

Indiana Gas Association sponsored this project through Purdue Research Foundation.

NOTATION

a_i = activity of component i at T and p of solution, $a_i = 1.0$ at $x_i = 1.0$
f = functionality of solvent, active sites per molecule
f_R° = fugacity of pure liquid R at T and p of solution
f°_{RG} = fugacity of pure gaseous R at T and p of solution
ΔH_R° = standard enthalpy of reaction, k.cal./g. mole of complex
$\Delta \overline{H}_R$ = partial molal enthalpy change of component R in mixture
ΔH_T^M = total enthalpy change of mixture on mixing at constant T and p, cal.
ΔH^m = heat of mixing at constant T and p, cal./g. mole of solution
n_i = moles of component i
p = pressure
p_{RG} = partial pressure of refrigerant vapor, lb./sq.in.abs.
p°_{RG} = vapor pressure of pure refrigerant, lb./sq.in.abs.
T = absolute temperature, °K.
x_i = liquid mole fraction of component i
γ_i = activity coefficient of component i, $\gamma_i = 1.0$ at $x_i = 1.0$

LITERATURE CITED

1. Albright, L. F., P. C. Buclez, C. R. Pluche, and T. C. Doody, *Am. Soc. Heating, Refrig., Air-Conditioning Engrs. Trans.*, **66**, 423 (1960).
2. Albright, L. F., and J. D. Lawyer, *Am. Soc. Heating, Refrig., Air-Conditioning Journal*, **1**, No. 4, p. 67 (1959).
3. Albright, L. F., and A. S. Mandelbaum, *Refrig. Eng.*, **64**, No. 10, p. 37 (1956).
4. E. I. duPont de Nemours and Co., Inc., bulletin, Thermodynamic Properties of Freon-21 (1939); Thermodynamic Properties of Freon-22 (1945); and Private communication from J. J. Martin, University of Michigan, Ann Arbor, Michigan (1960).
5. Mastrangelo, S. V. R., *J. Phys. Chem.*, **63**, 608 (1959).
6. ———, *Am. Soc. Heating, Refrig., Air-Conditioning Engrs. Journal*, **1**, No. 10, p. 64 (1960).
7. Terrier, Francois, M.S. thesis, Purdue Univ., Lafayette, Indiana (1961).
8. Thieme, A. A., and L. F. Albright, *Am. Soc. Heating, Refrig., Air-Conditioning Journal*, **3**, No. 7, p. 71 (1961).
9. Zellhoefer, G. F., and M. J. Marvel, *J. Am. Chem. Soc.*, **60**, 1343 (1938).

Manuscript received December 1, 1961; revision received March 5, 1962; paper accepted March 7, 1962. Paper presented at A.I.Ch.E. New Orleans meeting.

Drop Formation from Rapidly Moving Liquid Sheets

R. P. FRASER, PAUL EISENKLAM, NORMAN DOMBROWSKI, and DAVID HASSON
Imperial College, London, England

In a widespread range of spraying applications atomization is achieved by a nozzle which transforms the liquid into an unstable sheet.

A former investigation of spray sheets in atmosphere (*1*) has established two principal modes of disintegration. Within a limited range of conditions sheets may remain undisturbed and disintegrate into a network of unstable ligaments produced by the coalescence of expanding perforations. A sheet is however normally disturbed by aerodynamic waves. Fragments of liquid are broken off the wavy sheet and, although suffering continuous disintegration by air action, tend to contract into unstable ligaments.

The ambient atmosphere is thus one of the significant factors contributing to the instability and disintegration of a liquid sheet. This investigation examines the separate effects of ambient atmosphere and liquid velocity on the mode of breakup of a sheet not rendered unstable by air action and determines the characteristic drop sizes resulting from sheets undergoing different modes of disintegration.

Flat spray sheets, produced by single-hole fan spray nozzles, have been selected for investigation because they are convenient for both analytical

---

David Hasson is presently with the Technicon, Haifa, Israel.