Predicting Gas-Liquid Diffusivities

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A new expression to predict the diffusivity of a gas in a liquid is compared to previously developed equations. The new expression appears to work as well or better than the other equations in most cases.

Diffusion in liquids has been studied for many years (*14*, *16*). Available expressions for calculating diffusion coefficients in liquids, however, only partially have been successful. There is no one equation which predicts diffusivities for all systems involving a liquid solvent.

The object of this investigation was to compare the existing diffusivity expressions for systems involving a gas solute diffusing through a liquid solvent. Dissolved gases form a special class of molecules of small size and low enthalpy of vaporization in the broad category of liquid diffusion and thus provide a good means of comparing the accuracy of the various equations.

The first equation used is the Stokes-Einstein equation developed as early as 1905 (*4*).

$$D_{AB} = \frac{kT}{6\,\pi\mu_B R_A} \tag{1}$$

where D_{AB} is the diffusion coefficient of A in B, k is the Boltzman constant, T is the absolute temperature, μ_B is the viscosity of solvent B, and R_A is the radius of the solute A particle.

This equation was developed from a hydrodynamic approach. Stokes law for drag on a spherical particle was employed as the retarding force.

Wilke and Chang (*34*), starting from the same approach came up with the expression:

$$D_{AB} = \frac{7.4 \times 10^{-8}\,(\chi_B M_B)^{1/2} T}{\mu_B V_A^{0.6}} \tag{2}$$

where M_B is the molecular weight of solvent B, V_A is the molar volume of solute A, and χ_B is the association number of the solvent which is 2.6 for water, 1.9 for methanol, 1.5 for ethanol, and 1.0 for unassociated substances. They have tested this equation for 251 pairs of systems and reported it to be accurate within ±10%. The main limitation is the association number which had to be calculated experimentally for associated systems.

Othmer and Thakar (*23*) observed that log D_{AB} is a linear function of log μ_B and proposed the empirical equation:

$$D_{AB} = \frac{1.4 \times 10^{-4}}{V_A^{0.6}\,\mu_B \mu_W^{1.1\frac{\Delta H_{\mathrm{vap}\,B}}{\Delta H_{\mathrm{vap}\,W}}}} \tag{3}$$

where μ_W is the viscosity of water at the temperature of interest $\Delta H_{\mathrm{vap}\,B}$ is the enthalpy of vaporization of the solvent B, and $\Delta H_{\mathrm{vap}\,W}$ is the enthalpy of vaporization of water.

Based on liquid structure and absolute rate theory approach, Eyring and co-workers (*9*, *12*, *25*, *26*) proposed the following equation:

$$D_{AB} = \frac{kT}{\xi_A \mu_B}\left(\frac{N}{V_B}\right)^{1/3} \exp\left(\frac{E_{\mu B} - E_{DAB}}{RT}\right) \tag{4}$$

where ξ_A is the number of B molecules around a central A molecule on the same plane, N is the Avogadro's number, V_B is the molar volume of the solvent, R is the gas constant, and $E_{\mu B}$ and E_{DAB} are the activation energies for viscosity and diffusion, respectively.

They assumed that $E_{\mu B} = E_{DAB}$ and $\xi_A = 6$. Thus

$$D_{AB} = \frac{kT}{6\,\mu_B}\left(\frac{N}{V_B}\right)^{1/3} \tag{5}$$

While these are rigorous assumptions for self-diffusion they are questionable for mutual diffusion.

Gainer and Metzner (*11*) proposed to calculate the activation energy difference from molecular interactions considering hydrogen bonding and dispersion forces. Unfortunately their method cannot be applied to gas-liquid systems.

Recently Akgerman (*1*) modified and extended Gainer and Metzner's study (*11*) to gas-liquid systems using absolute rate theory (*12*) and a significant liquid structure model (*9*). He proposed an equation of the form

$$D_{AB} = \frac{kT}{\xi_A \mu_B}\left(\frac{N}{V_B}\right)^{1/3}\left(\frac{M_B}{M_A}\right)^{1/2} \exp\left(\frac{E_{\mu B} - E_{DAB}}{RT}\right) \tag{6}$$

where M_A is the molecular weight of the solute A, and ξ_A, the number of molecules around the central A molecule, is given by:

$$\xi_A = 6\left(\frac{V_A}{V_B}\right)^{1/6} \tag{7}$$

Activation energy difference is calculated considering jumping energies associated with different molecules (*1*):

$$E_{\mu B} - E_{DAB} = E_{BB}^{j}\left\{1 - \left(\frac{E_{AA}^{j}}{E_{BB}^{j}}\right)^{1/(\xi_A+1)}\right\} \tag{8}$$

where E_{AA}^{j} and E_{BB}^{j} are the jumping energies for solute A and solvent B molecules, respectively. To calculate the activation energy of jumping for liquids, the expression given by Glasstone et al. (*12*) is used:

$$E_{BB}^{j} = -\frac{R\ln\left(\frac{\mu_2}{\mu_1}\right) + \frac{R}{2}\ln\left(\frac{T_2}{T_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} \tag{9}$$

where μ_1 and μ_2 are the viscosities of the solvent at temperatures T_1 and T_2.

Akgerman (*1*) proposed to calculate E_{AA}^{j} from the equation

$$E_{AA}^{j} = 5875.3\,M_A^{-0.186} \tag{10}$$

In his work molecular interactions between solute-solvent and solvent-solvent pairs are taken into consideration to calculate the activation energies. Table I, including 49 sys-

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Table I. Experimental and Calculated Diffusivities

Solute	Solvent	Temp, °C	Exptl diff D_{AB} × 10^5	A-G eq	W-C eq	S-E eq	Eyr. eq	O-T eq	Ref.
Oxygen	Water	10.0	1.54	−2	−1	52	−2	25	(*10*)
		10.0	1.70	7	7	57	7	32	(*35*)
		15.0	1.66	−10	−10	48	−10	7	(*5*)
		16.0	1.87	−0.1	−0.3	53	−0.6	13	(*14*)
		18.2	1.99	−0.7	−1	52	−1	8	(*14*)
		20.0	2.30	8	7	56	7	12	(*35*)
		20.0	2.01	−5	−5	50	−6	−0.3	(*5*)
		22.0	2.25	3	2	54	2	3	(*14*)
		22.0	2.22	2	1	54	1	2	(*14*)
		25.0	2.60	7	6	56	6	0.7	(*14*)
		25.0	2.41	0.3	0.9	53	−1	−7	(*5*)
		25.0	2.40	−0.04	−1	52	−1	−7	(*15*)
		25.0	2.41	0.3	−0.9	53	−1	−7	(*33*)
		25.0	2.07	−15	−17	45	−17	−24	(*8*)
		25.0	2.20	−9	−10	48	−10	−17	(*10*)
		29.6	3.49	23	21	63	21	8	(*19*)
		30.0	2.80	3	1	54	1	−15	(*35*)
		37.0	3.00	−5	−8	49	−8	−43	(*14*)
		40.0	3.80	11	8	57	8	−27	(*35*)
		40.0	3.33	−1	−4	51	−4	−45	(*10*)
		50.0	4.20	2	−1	52	−1	−65	(*35*)
		55.0	4.50	0.4	−3	51	−4	−82	(*10*)
		60.0	5.70	13	9	58	9	−71	(*35*)
Carbon dioxide	Water	6.5	1.14	−5	−3	48	−22	32	(*32*)
		6.5	1.08	−11	−9	45	−30	28	(*14*)
		10.0	1.17	−14	−13	43	−34	17	(*5*)
		10.0	1.28	−4	−3	48	−22	24	(*14*)
		10.0	1.30	−3	−1	48	−21	25	(*14*)
		15.0	1.40	−11	−10	44	−31	7	(*14*)
		15.0	1.39	−11	−11	44	−32	6	(*5*)
		15.8	1.49	−6	−5	46	−26	9	(*14*)
		16.0	1.57	−1	−0.8	49	−19	13	(*14*)
		16.0	1.63	2	2	51	−15	16	(*14*)
		16.4	1.57	−2	−2	48	−21	11	(*14*)
		18.0	1.71	1.57	1	50	−16	11	(*24*)
		20.0	1.77	−1	−1	49	−20	3	(*14*)
		20.0	1.62	−10	−10	44	−31	−5	(*5*)
		20.4	1.85	2	2	50	−16	6	(*14*)
		24.8	1.94	−4	−5	47	−25	−11	(*14*)
		25.0	1.87	−8	−9	44	−30	−16	(*10*)
		25.0	1.95	−4	−5	47	−25	−11	(*10*)
		25.0	1.92	−5	−6	46	−27	−13	(*10*)
		25.0	1.85	−10	−10	44	−31	−17	(*32*)
		25.0	1.98	−2	−3	48	−23	−9	(*8*)
		25.0	1.90	−7	−7	45	−28	−14	(*5*)
		30.0	2.29	0.0	−1	49	−20	−18	(*14*)
		30.0	2.25	−1	−3	48	−22	−21	(*5*)
		35.0	2.26	−13	−15	41	−37	−49	(*14*)
		35.0	2.17	−17	−20	39	−43	−54	(*32*)
		40.0	2.80	−1	−4	47	−24	−45	(*8*)
		40.0	2.75	−3	−6	46	−26	−48	(*14*)
		50.0	3.24	−7	−11	44	−32	−80	(*14*)
		52.0	3.61	0.8	−2	48	−22	−72	(*32*)
		65.0	4.29	−5	−10	44	−31	−126	(*32*)
Nitrogen	Water	10.0	1.29	−22	−7	47	−21	21	(*10*)
		10.0	1.80	12	22	62	12	43	(*35*)
		10.0	1.34	−17	−3	49	−17	24	(*14*)
		15.0	1.35	−35	−20	40	−36	−0.8	(*2*)
		15.0	1.78	−3	8	55	−3	23	(*2*)
		15.0	1.94	5	16	58	5	29	(*14*)
		17.5	1.62	−20	−7	47	−21	4	(*14*)
		20.0	2.60	18	27	64	17	31	(*35*)
		20.0	1.66	−27	−13	44	−28	−7	(*2*)
		20.0	2.08	−1	9	55	−2	13	(*2*)
		21.7	2.00	−10	1	51	−11	2	(*14*)
		22.0	2.02	−10	1	51	−11	−2	(*24*)
		24.0	2.10	−11	−0.2	50	−13	−4	(*14*)
		25.0	1.80	−33	−19	41	−35	−27	(*14*)
		25.0	1.83	−31	−17	42	−33	−25	(*14*)
		25.0	2.25	−6	4	52	−8	−1	(*14*)

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Table I. *(Continued)*

Solute	Solvent	Temp, °C	Exptl diff D_{AB} $\times 10^5$	A-G eq	W-C eq	S-E eq	Eyr. eq	O-T eq	Ref.
Nitrogen	Water	25.0	2.01	−19	−7	47	−21	−14	*(10)*
		25.0	1.94	−24	−11	45	−25	−18	*(2)*
		25.0	2.24	−7	3	52	−8	−2	*(2)*
		29.6	3.47	22	29	65	20	18	*(19)*
		30.0	3.50	22	30	65	21	18	*(35)*
		30.0	2.00	−35	−22	40	−37	−43	*(14)*
		37.0	2.70	−17	−6	47	−20	−41	*(14)*
		40.0	2.83	−19	−8	46	−22	−52	*(10)*
		40.0	4.30	21	28	64	19	−0.0	*(35)*
		50.0	5.10	19	25	63	16	−20	*(35)*
		55.0	3.80	−18	−9	46	−23	−91	*(10)*
		60.0	6.50	24	29	65	20	−33	*(35)*
Hydrogen	Water	10.0	4.60	12	51	80	65	64	*(35)*
		10.0	4.34	7	48	79	63	62	*(14)*
		15.0	3.67	−28	29	71	49	40	*(2)*
		16.0	4.73	−1	43	77	60	51	*(14)*
		17.0	5.20	4	47	78	62	53	*(5)*
		20.0	4.48	−22	32	73	52	36	*(2)*
		20.0	5.00	−9	39	75	57	42	*(35)*
		21.0	5.15	−8	40	76	57	41	*(14)*
		24.5	4.90	−26	30	72	50	27	*(14)*
		25.0	7.07	11	51	80	65	48	*(5)*
		25.0	4.80	−30	28	71	49	23	*(33)*
		25.0	5.30	−18	34	74	53	30	*(2)*
		26.0	6.80	5	47	79	63	43	*(7)*
		26.5	7.10	8	49	79	64	44	*(5)*
		30.0	7.00	−1	44	77	60	34	*(35)*
		40.0	8.30	−8	40	76	58	17	*(35)*
		50.0	9.70	−15	37	75	55	−1	*(35)*
		60.0	13.1	−3	44	77	60	−5	*(35)*
Chlorine	Water	10.0	0.91	−16	−17	35	−72	14	*(18)*
		10.0	0.97	−8	−10	39	−62	19	*(14)*
		13.0	0.98	−18	−20	33	−77	4	*(18)*
		15.0	1.14	−7	−9	39	−61	8	*(14)*
		15.0	1.13	−8	−10	38	−62	7	*(5)*
		18.3	1.20	−11	−14	36	−68	−4	*(18)*
		20.0	1.22	−15	−19	34	−74	−12	*(18)*
		22.4	1.32	−13	−16	35	−71	−17	*(18)*
		25.0	1.42	−12	−16	35	−71	−24	*(18)*
		25.0	1.40	−14	−18	34	−74	−25	*(15)*
		25.0	1.51	−6	−9	39	−61	−16	*(14)*
		25.0	1.48	−8	−12	38	−64	−19	*(14)*
		30.0	1.62	−11	−15	36	−70	−36	*(18)*
		30.0	1.74	−3	−7	40	−58	−26	*(14)*
		35.0	1.81	−11	−17	35	−72	−50	*(18)*
Carbon monoxide	Water	10.0	1.07	−47	−31	35	−47	4	*(36)*
		20.0	2.03	−4	6	54	−5	10	*(36)*
		30.0	2.43	−11	−1	50	−13	−19	*(36)*
		40.0	3.62	6	14	58	3	−20	*(36)*
		50.0	4.11	−0.7	6	54	−4	−51	*(36)*
		60.0	5.68	12	18	60	9	−54	*(36)*
Nitric oxide	Water	10.0	1.55	−5	−6	51	−1	22	*(36)*
		20.0	2.07	−5	−7	50	−3	−2	*(36)*
		30.0	3.96	29	27	66	30	14	*(36)*
		40.0	5.16	32	29	67	32	1	*(36)*
		50.0	9.38	54	52	78	54	22	*(36)*
		60.0	13.6	62	60	81	62	24	*(36)*
Nitrous oxide	Water	15.0	1.62	5	8	53	−13	23	*(5)*
		16.2	1.56	−0.6	2	50	−21	15	*(14)*
		20.0	2.11	16	18	58	−1	22	*(5)*
		20.0	1.58	−11	−9	44	−35	−3	*(31)*
		25.0	2.57	21	23	50	5	18	*(5)*
		25.0	1.69	−18	−16	40	−44	−23	*(8)*
		40.0	2.55	−10	−10	43	−36	−53	*(8)*
Sulfur dioxide	Water	20.0	1.40	−6	−8	41	−52	−3	*(14)*
		20.0	1.46	−1	−4	43	−46	1	*(14)*
		20.0	1.66	10	8	50	−28	13	*(14)*
		20.0	1.62	8	6	49	−31	10	*(14)*
		25.0	2.04	17	14	53	−19	9	*(14)*
		25.0	1.83	7	5	48	−33	−0.8	*(14)*

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Table I. *(Continued)*

Solute	Solvent	Temp, °C	Exptl diff D_{AB} $\times 10^5$	A-G eq	W-C eq	S-E eq	Eyr. eq	O-T eq	Ref.
Sulfur dioxide	Water	30.0	2.08	8	5	48	−32	−11	(*14*)
		30.0	1.89	−0.1	−3	43	−45	−21	(*21*)
		35.0	2.33	8	4	48	−33	−22	(*14*)
		40.0	2.59	8	4	48	−34	−33	(*14*)
Helium	Water	10.0	5.50	9	−99	60	71	−45	(*35*)
		15.0	5.68	−2	−126	55	67	−88	(*2*)
		15.0	7.65	23	−67	67	75	−40	(*2*)
		20.0	6.84	0.9	−117	57	68	−106	(*2*)
		20.0	8.95	24	−66	67	76	−57	(*2*)
		20.0	6.80	0.3	−118	57	68	−107	(*35*)
		24.0	8.30	8	−99	60	71	−107	(*7*)
		25.0	8.02	3	−112	58	69	−125	(*2*)
		25.0	9.50	18	−79	64	74	−90	(*2*)
		25.0	6.30	−23	−170	47	61	−186	(*33*)
		30.0	8.00	−9	−140	52	65	−182	(*35*)
		40.0	8.80	−26	−175	45	60	−285	(*35*)
		50.0	11.70	−17	−155	50	63	−315	(*35*)
		60.0	14.9	−11	−141	52	65	−358	(*35*)
Neon	Water	10.0	2.61	23	20	67	39	42	(*36*)
		20.0	3.00	10	6	61	28	11	(*36*)
		22.2	2.80	−1	−6	56	19	−6	(*14*)
		30.0	3.81	9	4	60	27	−11	(*36*)
		40.0	5.39	20	15	65	35	−18	(*36*)
		50.0	6.50	19	13	64	34	−40	(*36*)
		60.0	8.08	22	16	65	36	−59	(*36*)
Argon	Water	10.0	1.70	15	12	58	7	36	(*35*)
		15.0	1.43	−17	−21	42	−28	−1	(*2*)
		15.0	1.79	6	2	53	−2	18	(*2*)
		20.0	1.68	−14	−20	42	−27	−13	(*2*)
		20.0	1.94	0.5	−4	50	−10	1	(*2*)
		20.0	2.30	16	12	58	7	16	(*35*)
		25.0	1.92	−14	−20	42	−26	−27	(*2*)
		25.0	2.02	−8	−14	45	−20	−21	(*2*)
		25.0	2.00	−9	−15	45	−21	−22	(*8*)
		30.0	2.70	8	3	54	−2	−13	(*35*)
		40.0	3.80	19	13	58	8	−20	(*35*)
		50.0	4.80	22	15	59	10	−37	(*35*)
		60.0	6.70	33	27	65	22	−38	(*35*)
Krypton	Water	10.0	1.45	25	8	54	−8	33	(*36*)
		20.0	1.68	13	−6	46	−27	−1	(*36*)
		30.0	2.17	15	−6	46	−27	−25	(*36*)
		40.0	2.77	17	−5	46	−25	−47	(*36*)
		50.0	4.07	31	11	55	−5	−43	(*36*)
		60.0	5.54	40	21	60	6	−48	(*36*)
Xenon	Water	10.0	0.41	−115	−178	−49	−283	−102	(*36*)
		20.0	0.60	−95	−157	−38	−255	−144	(*36*)
		30.0	1.02	−46	−95	−5	−170	−130	(*36*)
		40.0	1.56	−18	−61	13	−123	−125	(*36*)
		50.0	2.77	19	−11	40	−54	−82	(*36*)
		60.0	3.98	33	6	49	−29	−78	(*36*)
Methane	Water	10.0	1.90	−0.1	24	63	17	44	(*35*)
		20.0	2.40	−6	18	60	11	22	(*35*)
		30.0	3.0	−9	15	59	8	1	(*35*)
		40.0	4.20	1	24	63	17	−5	(*35*)
		50.0	4.70	−7	16	59	9	−35	(*35*)
		60.0	6.70	9	29	65	22	−33	(*35*)
Ethane	Water	10.0	1.60	13	35	63	1	53	(*35*)
		15.0	1.40	−15	14	51	−31	28	(*2*)
		20.0	1.68	−10	16	53	−27	21	(*2*)
		20.0	2.30	19.0	39	65	7	42	(*35*)
		25.0	1.71	−23	6	47	−42	0.9	(*2*)
		25.0	1.88	−12	15	52	−29	9	(*2*)
		30.0	2.80	14	35	63	1	24	(*35*)
		40.0	3.80	21	40	66	8	16	(*35*)
		50.0	4.10	11	31	61	−4	−11	(*35*)
		60.0	4.90	11	31	61	−5	−30	(*35*)
Propane	Water	10.0	1.30	13	36	60	−21	53	(*35*)
		20.0	1.80	15	37	61	−18	40	(*35*)
		30.0	2.40	19	39	62	−14	28	(*35*)

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Table I. *(Continued)*

Solute	Solvent	Temp, °C	Exptl diff D_{AB} × 10^5	A-G eq	W-C eq	S-E eq	Eyr. eq	O-T eq	Ref.
Propane	Water	40.0	2.70	10	32	58	−28	5	*(35)*
		50.0	3.50	15	35	60	−22	−4	*(35)*
		60.0	4.40	20	38	61	−17	−17	*(35)*
n-Butane	Water	10.0	0.83	−16	14	43	−89	37	*(35)*
		20.0	1.40	7	31	54	−52	34	*(35)*
		30.0	1.90	12	34	56	−45	23	*(35)*
		40.0	2.50	17	37	58	−39	12	*(35)*
		50.0	3.30	23	41	61	−29	4	*(35)*
		60.0	4.30	30	45	64	−20	−2	*(35)*
Nitrogen dioxide	Water	20.0	1.23	−45	−52	25	−73	−44	*(17)*
		30.0	1.59	−43	−52	25	−73	−78	*(17)*
Hydrogen sulfide	Water	15.5	1.43	−20	−11	44	−30	5	*(14)*
		16.0	1.77	1	8	54	−6	21	*(14)*
		25.0	1.36	−64	−53	23	−79	−63	*(14)*
Acetylene	Water	0.0	1.10	−0.9	14	57	−1	54	*(29)*
		10.0	1.50	−3	10	55	−4	35	*(29)*
		17.5	1.69	−14	0.5	50	−16	11	*(29)*
		30.0	2.19	−22	−7	46	−25	−25	*(29)*
Carbon dioxide	Ethanol	6.40	2.45	50	45	77	63	70	*(22)*
		10.0	2.78	53	47	78	65	68	*(22)*
		15.0	3.02	51	46	77	64	63	*(22)*
		20.0	3.40	52	46	78	64	58	*(22)*
		25.0	3.42	46.9	40	75	60	48	*(6)*
		30.0	3.78	47	40	75	60	43	*(6)*
		30.0	4.05	50	44	77	63	47	*(30)*
		30.0	3.69	45	38	75	59	42	*(20)*
Carbon dioxide	*n*-Heptane	25.0	6.03	30	−7	63	57	24	*(6)*
Carbon dioxide	*i*-Butyl alcohol	25.0	2.20	20	64	87	83	73	*(6)*
Carbon dioxide	Amyl alcohol	25.0	1.91	18	61	87	84	73	*(6)*
Oxygen	Ethanol	29.6	2.64	11	−0.4	61	43	5	*(19)*
Oxygen	Benzene	29.6	2.89	−37	−72	37	21	−46	*(19)*
Oxygen	Cyclohexane	29.6	5.31	27	34	77	73	46	*(19)*
Hydrogen	Carbon tetrachloride	0.0	6.28	−12	39	86	86	78	*(27)*
		25.0	9.82	−19	37	86	85	64	*(27)*
		25.0	10.5	−11	41	87	86	66	*(28)*
Nitrogen	Carbon tetrachloride	0.0	2.44	−28	2	73	64	65	*(27)*
		25.0	3.40	−45	−13	69	59	35	*(27)*
		25.0	3.42	−44	−12	69	59	36	*(3)*
Argon	Carbon tetrachloride	0.0	2.44	−18	−4	72	64	63	*(27)*
		25.0	3.63	−25	−13	70	62	35	*(27)*
Methane	Carbon tetrachloride	0.0	2.05	−80	−20	67	58	57	*(27)*
		25.0	2.89	−104	−37	63	52	21	*(27)*
Oxygen	Carbon tetrachloride	25.4	2.71	−33	−17	69	62	32	*(1)*
Nitrogen	Benzene	25.0	6.93	46	41	77	69	52	*(3)*
Ethane	*n*-Hexane	30.0	6.01	2.54	−8	55	37	12	*(20)*
Ethane	*n*-Heptane	30.0	5.60	10	1	61	49	24	*(20)*
Helium	Ethanol	29.6	14.3	52	−29	79	89	−21	*(19)*
Sulfur dioxide	*n*-Heptane	20.0	2.70	−24	−95	27	8	−26	*(13)*
Sulfur dioxide	*n*-Nonane	20.0	2.50	4.56	−41	53	45	18	*(13)*
Sulfur dioxide	*n*-Decane	20.0	2.40	15	−19	62	57	34	*(13)*
Methane	Glycerol	25.4	0.95	−20	99	99	99	99	*(1)*
Hydrogen	*n*-Hexane	25.4	16.36	−5	18	76	78	38	*(1)*
Hydrogen	Cyclohexane	25.4	7.08	−17	36	81	81	50	*(1)*
Hydrogen	Ethylene glycol	25.4	0.75	−60	63	90	88	72	*(1)*
Hydrogen	Methanol	20.0	16.50	52	67	87	83	70	*(28)*
Hydrogen	Ethanol	20.0	15.10	67	79	93	91	84	*(28)*
Hydrogen	*n*-Propanol	25.0	11.90	63	81	94	94	85	*(28)*
Hydrogen	*i*-Butyl alcohol	20.0	7.90	57	85	96	96	90	*(28)*
Hydrogen	Amyl alcohol	20.0	20.40	83	94	98	98	96	*(28)*

tems and over 250 data points, summarizes the results obtained in applying the presented equations to gas-liquid systems. The experimental diffusivities given under the heading "Exptl Diff" are in units cm²/sec. In presenting the data, percent deviations from the experimental values are reported for each equation. The percent deviation is defined as

$$\% \text{ deviation} = \frac{\text{experimental value} - \text{calculated value}}{\text{experimental value}} \times 100$$

The column heading "A-G Eq" stands for percent deviation between the experimental and calculated values using Equations 6–10, "W-C Eq" using Wilke-Chang Equation, "S-E Eq" using Stokes-Einstein Equation, "Eyr. Eq" using Eyring Equation, and "O-T Eq" using Othmer and Thakar Equation. References to individual data points are given in the last column. Computer readout tables have been deposited with the American Chemical Society Microfilm Depository Service.

As can be seen from Table I, the equation proposed by

Akgerman (*1*) based on significant liquid structure and absolute rate theory works better than all the other expressions. The Wilke-Chang Equation, although as accurate for many systems, is inaccurate when the solute is a small molecule like hydrogen or helium or when solvent is a viscous liquid. The Stokes-Einstein and the Eyring equations are inaccurate, perhaps due to the questionable assumptions in their derivations leading to the final expressions. The Othmer and Thakar expression, on the other hand, cannot predict the temperature dependency of diffusion coefficients and is inaccurate for nonaqueous solvents.

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Solubility of Hydrohalogens in Normal C_5–C_{16} Alcohols

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Data on the solubility of HBr and HCl in n-C_5–C_{16} alcohols are presented. Heat of solution of HBr into the above alcohols in the temperature range of 100–60°C is about 10,500 cal/mol.

Higher molecular weight alkyl halides, such as lauryl bromide and cetyl chloride, are used in making detergents and germicides (*1, 4, 9, 10*). One method of making these alkyl halides is to react hydrogen bromide and hydrogen chloride gases with the corresponding alcohols at temperatures on the order of 120–60°C. The solubility of HBr and HCl in these alcohols must be known in order to interpret the kinetic data of the absorption of HBr and HCl. Fernandes and Sharma (*2*) have reported the solubility of HCl in n-C_{12}–n-C_{18} alcohols in the temperature range of 30–200°C. Ionin et al. (*8*) and Gerrard et al. (*6*) have reported solubilities of HCl in n-C_1–n-C_{10} alcohols at temperatures up to 60°C and of HBr in n-octanol and so forth at only one temperature of 15°C. There is no other information available for the solubility of HBr in alcohols higher than n-C_8 and also at higher temperatures. In this work, data on the solubility of HBr in n-C_5–n-C_{18} alcohols in the temperature range of 15–160°C are presented.

MATERIALS

HBr gas supplied by Matheson Co. was of 99.8% purity (99% min purity). Alcohols supplied by K and K Labora-

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