ACKNOWLEDGMENT

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LITERATURE CITED

(1) Campaigne, E., Osborn, S.W., *J. Org. Chem.* **22**, 561 (1957).
(2) Dalgliesh, C.E., Mann, F.G., *J. Chem. Soc.* **1947**, p. 559.
(3) Gordella, G., Passerini, R., *Boll. sci. fac. chim. ind. Bologna* **14**, 104 (1956); *CA.* **53**, 17949i (1959).
(4) Holt, H.S., Reid, E.E., *J. Am. Chem. Soc.* **46**, 2333 (1924).
(5) Kaslow, C.E., Stayner, R.D., *Ibid.* **68**, 2600 (1946).
(6) Livingstone, S.E., *J. Chem. Soc.* **1956**, p. 437.
(7) Parham, W.E., Stright, P.L., *J. Am. Chem. Soc.* **78**, 4783 (1956).

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Diffusion Coefficients in Hydrocarbon Systems

The *n*-Butane–*n*-Decane System in the Liquid Phase

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Measurements of the Chapman-Cowling diffusion coefficient were carried out at pressures up to 600 p.s.i.a. at temperatures between 220° and 340° F. in the liquid phase of the *n*-butane–*n*-decane system. The Chapman-Cowling diffusion coefficient yielded much smaller variations with state than did the Fick diffusion coefficients. The relationships between these two types of coefficients are included.

EXPERIMENTAL INFORMATION available concerning the molecular transport of the lighter hydrocarbons in the liquid phase of binary hydrocarbon systems indicates that there is a significant variation in the Chapman-Cowling diffusion coefficient (*2*) for a particular binary system with changes in state. As a result of this variation it is desirable to carry out experimental investigations to establish the value of the Chapman-Cowling diffusion coefficient over the range of conditions of industrial interest. The current investigation relates to the molecular transport in the liquid phase of the *n*-butane-*n*-decane system at pressures up to nearly 600 p.s.i.a. in the temperature interval between 220° and 340° F.

METHODS AND EQUIPMENT

The experimental approach involved the introduction of *n*-butane in the gas phase at a known rate into an isochoric chamber containing a heterogeneous mixture of *n*-butane and *n*-decane. Initially, this binary mixture was brought to physical equilibrium by mechanical agitation. After quiescent conditions had been obtained, the pressure was increased a predetermined amount by addition of *n*-butane. The quantity of the lighter hydrocarbon required to maintain the system under isobaric conditions at the newly established elevated pressure was determined as a function of time.

The equipment has been described (*10, 12*). Small vertical tubes were provided in the lower part of the isochoric vessel to decrease the influence of local accelerations upon the molecular transport. The temperature was determined by a strain-free, platinum resistance thermometer (*4*) and was known relative to the international platinum scale within 0.02° F.

Pressure was measured by a balance involving a piston-sleeve combination and was known within 0.1 p.s.i.a. or 0.05 per cent, whichever was the larger measure of uncertainty. Isobaric conditions were maintained by means of a manostat (*15*). The *n*-butane was introduced in the liquid phase by an injector (*10*). Liquid *n*-butane was evaporated by passage through a conditioning coil of small dimensions located in the oil bath surrounding the isochoric vessel. Physical values of the position of the injector were recorded automatically as a function of time. The rate of introduction of *n*-butane was controlled from an analog output of the manostat. Variations in pressure during a set of diffusion measurements were not more than 0.05 p.s.i.a. No difficulties were experienced from the evaporation of the *n*-butane in the conditioning coil prior to its introduction into the diffusion vessel.

Methods of analysis used in other studies (*8*) were applied in the resolution of the experimental data. From the assumption of local equilibrium (*3*) at the gas-liquid interface, the following expression may be derived (*8*) to establish the Chapman-Cowling diffusion coefficient:

$$D_{Ckj} = \left[\frac{\pi \underline{m}_{kc}^{2}}{4A_{i}^{2}\theta(\sigma_{kb} - \sigma_{kbo})^{2}}\right]\left[1 - \frac{\overline{V}_{kl}^{*}(\sigma_{kb} - \sigma_{kd})}{1 - \overline{V}_{kl}^{*}\sigma_{kd} - \overline{V}_{jl}^{*}\sigma_{jd}}\right]^{2} \quad (1)$$

In the foregoing expression the asterisks indicate values of the quantity in question for the conditions existing in the liquid phase at bubble point during a particular set of isobaric, isothermal measurements. The effect of hydrodynamic velocity (*10*) and the change in volume of the liquid phase were taken into account. Equation 1 is limited to a system where the state of the liquid phase at the interface is established from its prevailing temperature and pressure. Measurements obtained at physical equilibrium (*9, 11*) were employed to evaluate the partial volumetric data in the liquid and gas phases.

The value of the second bracketed term of Equation 1 as a function of pressure for the several temperatures investigated is depicted in Figure 1. The information is based on available volumetric and phase equilibrium data (*6, 11, 14*). At a temperature below the critical temperature of *n*-butane this term reaches a value of zero at the vapor pressure of *n*-butane and a value of unity at the vapor pressure of *n*-decane. Above the critical temperature of *n*-butane it assumes a value of unity at the critical pressure of the binary system. In the application of these values the state associated with the interface during the diffusion process was employed. Except near the critical state of the binary system the use of the partial volumetric behavior at the state corresponding to that at the interface did not introduce more than one per cent uncertainty in the results. If an attempt were made to take into account the variation in the partial specific volumes of the components in the transport path, the analysis of the measurements could be made only by use of numerical integration. The choice of the properties at the interface was made because the maximum molecular flux is encountered there and the state was known with the greatest certainty. It should be recognized that only small changes in state are involved in the entire transport path.

MATERIALS

The *n*-butane employed was research grade from the Phillips Petroleum Co. The sample was reported to contain less than 0.0009 mole fraction of impurities. Such a degree of purity was confirmed by the uniformity of vapor pressure as a function of quality near bubble point. The *n*-decane was obtained from the same source as research grade and was reported to contain less than 0.0065 mole fraction of impurities. The index of refraction of the *n*-decane at 77° F. relative to the D-lines of sodium was 1.4097. This value compares favorably with 1.40967 reported by Rossini (*1*) for an air-saturated sample at the same temperature. The specific weight of the *n*-decane at atmospheric pressure at 77° F. was 45.3394 pounds per cubic foot as compared to a value of 45.337 pounds per cubic foot reported (*1*) for an air-saturated sample at the same temperature. The agreement of these values of the index of refraction and specific weight of the sample of *n*-decane lends credence to the reported purity of this material. Throughout the entire experimental program the *n*-decane and *n*-butane were introduced into the isochoric diffusion vessel and other parts of the apparatus by conventional high vacuum techniques.

EXPERIMENTAL RESULTS

Following the assumptions involved in the derivation of Equation 1, the weight of *n*-butane added should be linear with respect to the square root of time, as long as the quantity of *n*-butane crossing the interface is less than half of that required to re-establish physical equilibrium at the higher pressures (*7*). Figure 2 is a typical set of experimental results showing the weight of *n*-butane added as a function of the square root of time. The value of the slope of the linear relationship of the weight of *n*-butane to the square root of time was established from the experimental measurements by conventional least squares techniques. The information shown in Figure 2 applies to the situation involving an initial pressure of 247.8 p.s.i.a. and weight fraction 0.450 *n*-butane at 280° F. The final pressure was 265.4 p.s.i.a. and the final equilibrium weight fraction *n*-butane was 0.493. The standard error of estimate for the data shown between $\theta_1^{1/2}$ and $\theta_2^{1/2}$ was 17.8×10^{-6} pound of *n*-butane, assuming all the error lies in the latter variable and none in the time.

Table I depicts an example of experimental measurements which were obtained. As a result of the relatively large enthalpy change associated with the solution of *n*-butane it was not possible to obtain substantially isothermal conditions in the liquid phase in times less than 1800 seconds after the increase in pressure. The weight of *n*-butane added was arbitrarily taken equal to zero at some appropriate time after the initial thermal gradients had disappeared.

A summary of the experimental results is set forth in Table II. The tabulation presents the final composition and concentration of *n*-butane, the quotient of the weight of *n*-butane added with respect to time, the correction factor, and the Chapman-Cowling diffusion coefficient. A

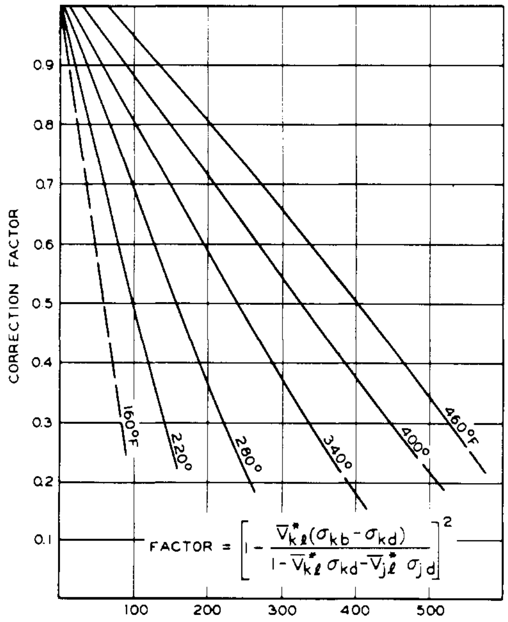

Figure 1. Correction factor for the *n*-butane–*n*-decane system

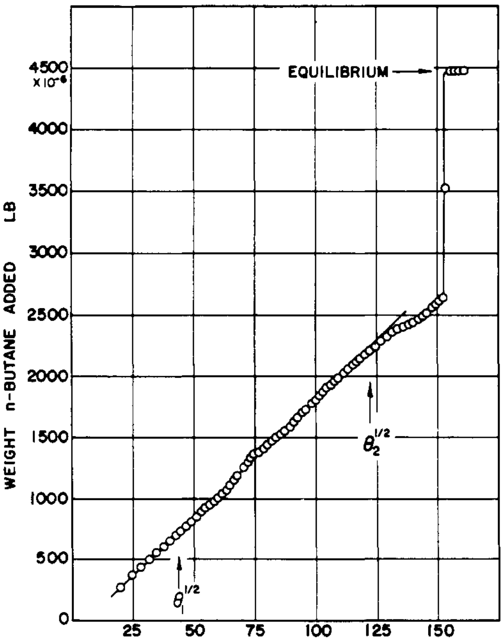

Figure 2. Typical experimental measurements at 280° F.

total of eight satisfactory measurements of the diffusion coefficient were made. The *n*-butane–*n*-decane system represents about the limit of satisfactory measurement of molecular transport by the methods employed. The large enthalpy changes associated with the solution of *n*-butane cause some local temperature gradients that are not conducive to the most accurate measurements. For this reason the study was limited to the range of conditions indicated in Table II.

The effect of pressure upon the Chapman-Cowling diffusion coefficient in the liquid phase of the *n*-butane–*n*-decane system constitutes Figure 3. The standard error of estimate associated with the deviation of the experimental values of the Chapman-Cowling diffusion coefficient from the smooth curves was 0.9×10^{-8} square foot per second. The linear deviation with regard to sign for the points shown was -0.2×10^{-8} square foot per second. The values decrease regularly from a maximum at the vapor pressure of *n*-decane, which corresponds to the behavior in an infinitely dilute solution. At the lower temperatures the two-phase region is limited by the vapor pressure of *n*-butane. Experimental measurements were not obtained at 280° F. at pressures above 270 p.s.i.a. Isobaric variation in the Chapman-Cowling diffusion coefficient with temperature is shown in Figure 4.

Smoothed values of the Chapman-Cowling diffusion coefficient in the liquid phase of the *n*-butane–*n*-decane system are set forth in Table III for a series of pressures and temperatures. The corresponding composition of the

Table I. Typical Experimental Results at 280° F.

Pressure, P.S.I.A.	247.8[a]	265.4[b]
Weight Fraction *n*-Butane	0.450[a]	0.493[b]

Time, Sec.	Weight of *n*-Butane Added,[c] Lb.	Time, Sec.	Weight of *n*-Butane Added,[c] Lb.
0	...	2,002	731.165
399	270.802×10^{-6}	2,202	769.851
603	367.517	2,402	808.537
803	437.152	2,602	851.092
1,003	495.181	2,800	893.646
1,203	557.078	3,000	924.595
1,402	599.633	...[d]	...[d]
1,602	649.925	26,000	4479.84×10^{-6}
1,802	696.348		

[a] Initial equilibrium pressure and composition. [b] Constant operating pressure and associated composition at interface during transport. [c] Weight added to heterogeneous isochoric system. [d] There were 78 similar entries at times between 3000 and 26,000 seconds.

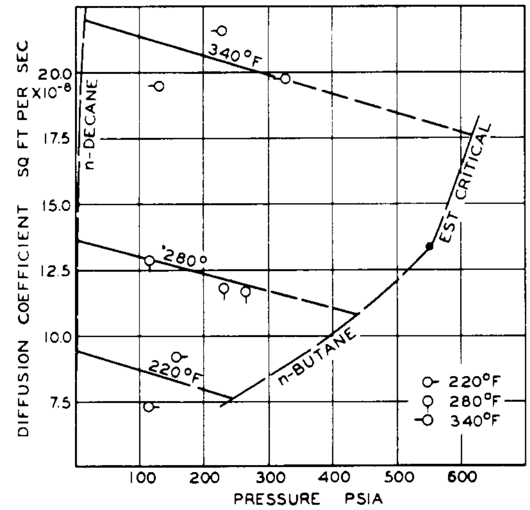

Figure 3. Influence of pressure on Chapman-Cowling diffusion coefficient

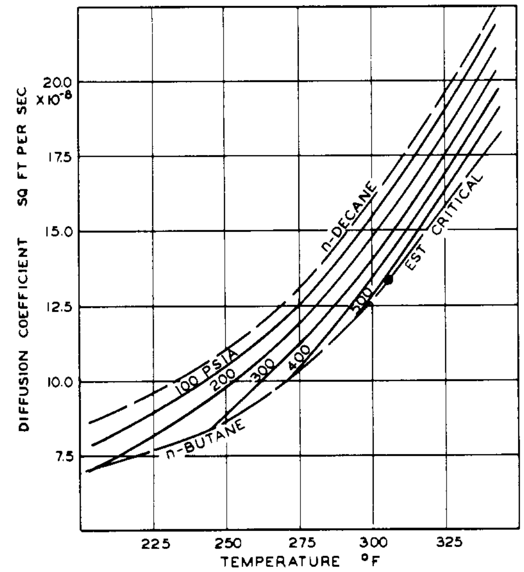

Figure 4. Effect of temperature on Chapman-Cowling diffusion coefficient

Table II. Summary of Experimental Results

Pressure, P.S.I.A. Initial	Pressure, P.S.I.A. Final	Composition *n*-Butane, Weight Fraction	Concentration *n*-Butane, Lb./Cu. Ft.	$(\Delta \overline{m}_k)^2/\theta$, Lb.²/Sec.[a]	Standard Error of Estimate, Lb.	Correction Factor	Chapman-Cowling Diffusion Coefficient, Sq. Ft./Sec.
				220° F.			
98.8	112.5	0.303	11.61	254.5×10^{-12}	6.10×10^{-6}	0.426	7.33×10^{-8}
139.6	158.4	0.505	17.74	1299.67	5.7	0.220	9.24
				280° F.			
100.0	115.5	0.168	6.32	83.19×10^{-12}	13.1×10^{-6}	0.641	12.92×10^{-8}
213.9	232.5	0.413	14.09	300.99	3.6	0.272	11.84
247.8	265.4	0.493	16.24	368.64	17.8	0.184	11.65
				340° F.			
109.7	130.6	0.119	4.27	78.94×10^{-12}	2.9×10^{-6}	0.736	19.51×10^{-8}
205.5	230.0	0.238	8.13	176.41	10.8	0.522	21.65
302.0	326.2	0.372	11.87	238.67	8.4	0.325	19.83

[a] Effective cross-sectional area = 0.019187 sq. ft.

Table III. Chapman-Cowling and Fick Diffusion Coefficients

Pressure, P.S.I.A.	Composition *n*-Butane, Weight Fraction	Specific Volume, Cu. Ft./Lb.	Partial Volume *n*-Decane, Cu. Ft./Lb.	Concentration *n*-Butane, Lb./Cu. Ft.	Diffusion Coefficients: Chapman-Cowling,[a] sq. ft./sec.	Diffusion Coefficients: Fick, *n*-butane,[a] sq. ft./sec.
			220° F.			
1.6[b]	0	0.0239	0.0239	0	9.4×10^{-8}	9.4×10^{-8}
50	0.107	0.0247	0.0239	4.34	9.1	9.4
100	0.257	0.0259	0.0236	9.94	8.7	9.5
150	0.465	0.0280	0.0229	16.62	8.3	10.2
200	0.733	0.0312	0.0215	23.48	7.9[c]	11.5[c]
241.2[d]	1.000	0.0349	0.0201	28.66	7.6	13.2
			280° F.			
5.1[b]	0	0.0248	0.0248	0	13.6×10^{-8}	13.6×10^{-8}
50	0.062	0.0254	0.0248	2.43	13.3	13.6
100	0.141	0.0262	0.0248	5.38	13.0	13.7
150	0.233	0.0272	0.0246	8.56	12.7	14.0
200	0.338	0.0284	0.0241	11.90	12.3	14.5
250	0.455	0.0298	0.0232	15.25	12.0	15.4
300	0.587	0.0319	0.0215	18.43	11.7[c]	17.4[c]
350	0.729	0.0346	0.0185	21.10	11.4	21.3
400	0.881	0.0387	0.0129	22.76	11.0	33.0
436.0[d]	1.000	0.0430	0.0061	23.24	10.8	77.4
			340° F.			
13.5[b]	0	0.0260	0.0260	0	21.9×10^{-8}	21.9×10^{-8}
50	0.035	0.0264	0.0260	1.29	21.7	22.0
100	0.086	0.0271	0.0260	3.16	21.4	22.3
150	0.141	0.0279	0.0259	5.06	21.0	22.6
200	0.200	0.0287	0.0258	6.96	20.6	23.1
300	0.334	0.0307	0.0248	10.88	19.9	24.6
400	0.485	0.0334	0.0225[c]	14.51	19.2[c]	28.5[c]
500	0.654	0.0378	0.0161	17.30	18.4	43.2
600	0.842	0.0519	...	16.23	17.7	...
616.3[e]	0.898	0.0647	...	13.89	17.6	...

[a] It should be recognized that the Chapman-Cowling diffusion coefficient exhibits the same numerical value for each of the components, while the Fick diffusion coefficient differs numerically for *n*-butane and *n*-decane at the same state. [b] Vapor pressure of *n*-decane (*9*). [c] Values at this and higher pressures were extrapolated from data at lower pressures. [d] Vapor pressure of *n*-butane (*5*). [e] Critical pressure of *n*-butane–*n*–decane system.

liquid phase expressed in weight fraction *n*-butane, and the concentration of *n*-butane in the liquid phase expressed in pounds per cubic foot have been included for each state. The values recorded in Table III correspond to the smooth curves presented in Figures 3 and 4.

The Fick diffusion coefficient for *n*-butane and *n*-decane may be related to the values of the Chapman-Cowling coefficient for the system by means of the following expressions:

$$D_{F,4} = D_{CC_{ij}}(V_l/\bar{V}_{10,l}) \tag{2}$$

$$D_{F,10} = D_{CC_{ij}}(V_l/\bar{V}_{4,l}) \tag{3}$$

Utilizing values of the partial volume of *n*-butane and of *n*-decane which are already available (*6*), values of the Fick diffusion coefficient were calculated. The values of the Fick diffusion coefficient recorded in Table III involve added uncertainties beyond those present in the values for the Chapman-Cowling coefficient because of uncertainties in the partial volume of *n*-decane at high weight fractions of *n*-butane. The variation in the Fick diffusion coefficient with bubble-point pressure is shown in Figure 5. The latter figure, when compared with Figure 3, indicates the much more rapid change in the Fick diffusion coefficient with state than is found for the Chapman-Cowling diffusion coefficient. Such rapid variation with change in state in this binary system indicates the limitation of the Fick coefficient in predicting the molecular transport in the liquid phase of this hydrocarbon system.

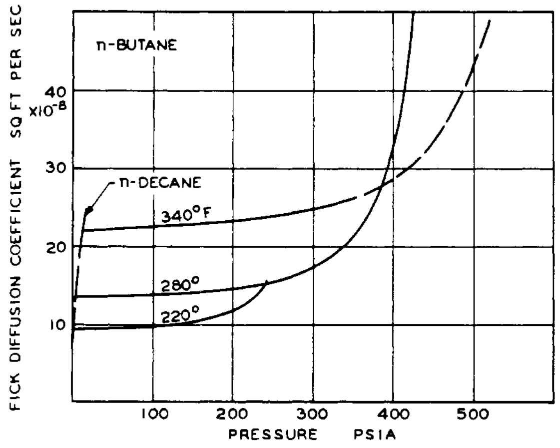

Figure 5. Influence of pressure on Fick diffusion coefficient for *n*-butane

ACKNOWLEDGMENT

This work is a contribution from Project 37 of the American Petroleum Institute at the California Institute of Technology. Virginia Berry contributed to the calculations and B. Lawson Miller to the preparation of the manuscript.

NOMENCLATURE

A_i = interfacial area, sq. ft.
D_{Ckj} = Chapman-Cowling diffusion coefficient for components k and j, sq. ft./sec.
$D_{F,4}$ = Fick diffusion coefficient for *n*-butane, sq. ft./sec.
$D_{F,10}$ = Fick diffusion coefficient for *n*-decane, sq. ft./sec.
m = total material, lb.
$\bar{V}$ = specific volume, cu. ft./lb.
$\bar{V}$ = partial specific volume of a component, cu. ft./lb.
Δ = difference in
σ_k = concentration of component k, lb./cu. ft.
θ = time, sec.

Subscripts

b = property evaluated at bubble-point conditions
c = transport into the cell
d = property evaluated at dew-point conditions
j = component j, the less volatile, or stagnant, component
k = component k, the more volatile, or diffusing, component
l = liquid phase
o = initial conditions
1,2 = state or condition

Superscript

* = average value of a property over the process considered

LITERATURE CITED

(1) Am. Petroleum Inst., Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons and Related Compounds."
(2) Chapman, Sydney, Cowling, T.G., "The Mathematical Theory of Non-Uniform Gases," 2nd ed., University Press, Cambridge, England, 1952.
(3) Kirkwood, J.G., Crawford, B., Jr., *J. Phys. Chem.* **56**, 1048 (1952).
(4) Meyers, C.H., *Bur. Standards J. Research* **9**, 807 (1932).
(5) Olds, R.H., Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **36**, 282 (1944).
(6) Olds, R.H., Sage, B.H., Lacey, W.N., "Fundamental Research on Occurrence and Recovery of Petroleum, 1948–1949," pp. 25–42, Am. Petroleum Inst., 1950.
(7) Pomeroy, R.D., Lacey, W.N., Scudder, N.F., Stapp, F.P., *Ind. Eng. Chem.* **25**, 1014 (1933).
(8) Reamer, H.H., Lower, J.H., Sage, B.H., J. CHEM. ENG. DATA **9**, 54 (1964).
(9) Reamer, H.H., Olds, R.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **34**, 1526 (1942).
(10) Reamer, H.H., Opfell. J.B., Sage, B.H., *Ind. Eng. Chem.* **48**, 275 (1956).
(11) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ibid.* **38**, 986 (1946).
(12) Reamer, H.H., Sage, B.H., J. CHEM. ENG. DATA **4**, 296 (1959).
(13) *Ibid.* **6**, 481 (1961).
(14) *Ibid.* **9**, 24 (1964).
(15) Reamer, H.H., Sage, B.H., *Rev. Sci. Instr.* **29**, 709 (1958).

RECEIVED for review May 21, 1962. Resubmitted March 16, 1964. Accepted June 1, 1964. Earlier publications from these laboratories on liquid diffusion are "Relations in Material Transport," Opfell and Sage, *Ind. Eng. Chem.* **47**, 918 (1955) and a series of articles, "Diffusion Coefficients in Hydrocarbon Systems," Reamer, Sage, and coworkers, *Ind. Eng. Chem.* **48**, 275, 282, 285 (1956); *A.I.Ch.E.J.* **3**, 449 (1957); *Ind. Eng. Chem., Chem. Eng. Data Ser.* **1**, 71 (1956); **3**, 54 (1958); J. CHEM. ENG. DATA **4**, 15, 296 (1959); **6**, 180, 481 (1961); **9**, 54 (1964).

CORRECTION:

In the article "Synthesis of *N*-(3′-Chloro-4′-methylphenyl)-2-methylpentanamide-1-C^{14}" by S.E. Forman and C.A. Erickson [J. CHEM. ENG. DATA **9**, 400 (1964)], a block of type has been inadvertently transposed. In column 1, page 401, under the bold heading *N*-(3′-Chloro-4′-methylphenyl)-2-methylpentanamide-1-C^{14}(VII), the material beginning with the eleventh line, "the aqueous solution was extracted with ether. This ether," through the twenty-second line, "by GPC and I.R. spectroscopy," should have appeared just before the bold heading and following the line, "that the chemical yield of IV was 77%. After acidification,".

CORRECTION:

In the article "A Study of the System $CaCl_2$-$ZnCl_2$-H_2O (NaCl Saturated) at 15° C." by E.P. Helvenston and E.A. Cuevas [J. CHEM. ENG. DATA **9**, 321 (1964)], in the third line of the Abstract, the weight per cent given for NaCl solubility should be 2.5 rather than 25%.