

for the calculation of normal stresses in laminar shearing flows of viscoelastic fluids. Unfortunately, it appears that the methods have not been used as carefully as necessary thus causing aberrations in the results.

#### NOTATION

$D$	= tube diameter
$d_j$	= jet diameter
$L$	= length of tube
$n'$	= $d(\ln \tau_w)/d(\ln 8v/D)$
$P_{ij}$	= components of deviatoric stress tensor
$p$	= isotropic stress pressure
$R$	= tube radius
$r$	= radius
$u$	= point velocity
$V$	= average velocity
$V_j$	= jet velocity
$x_i$	= orthogonal direction
$z$	= axial direction
$\tau_{ji}$	= component of stress tensor
$\tau_w$	= wall shear stress

#### LITERATURE CITED

1. Bagley, E. B., *Trans. Soc. Rheol.*, **5**, 355 (1961).
2. ———, S. H. Storey, and D. C. West, *J. Appl. Polymer Sci.*, to be published.
3. Brodnyan, J. G., F. H. Gaskins, W. Philippoff, and E. G. Lendrat, *ibid.*, **2**, 285 (1958).
4. Coleman, B. D., and W. Noll, *Arch. Rat. Mech. Anal.*, **3**, 289 (1959).
5. Gaskins, F. H., and W. Philippoff, *Trans. Soc. Rheol.*, **3**, 181 (1959).
6. ———, *J. Appl. Polymer Sci.*, **2**, 143 (1959).
7. Green, A. E., and R. S. Rivlin, *Arch. Rat. Mech. Anal.*, **1**, 1 (1957); **4**, 387 (1960); and R. S. Rivlin, *J. Rat. Mech. Anal.*, **5**, 189 (1956).
8. Kotaka, T., M. Kurata, and M. Tamura, *J. Appl. Phys.*, **30**, 1705 (1959); and *Bull. Chem. Soc. Japan*, **32**, 471 (1959).
9. Markovitz, H., *Trans. Soc. Rheol.*, **1**, 37 (1957).
10. Metzner, A. B., "Handbook of Fluid Dynamics," McGraw-Hill, New York (1961).
11. ———, E. L. Carley, and I. K. Park, *Mod. Plastics*, **37**, (11), 133 (1960).
12. Metzner, A. B., W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheol.*, **5**, 133 (1961).
13. Metzner, A. B., W. T. Houghton, R. E. Hurd, and C. C. Wolfe, "Proc. Int. Symp. on 2nd Order Effects in Elasticity, Plasticity and Fluid Dynamics," Jerusalem Academic Press, Jerusalem, Israel (1962).
14. Middleman, S., and J. Gavis, *Phys. Fluids*, **4**, 355 (1961).
15. *Ibid.*, p. 963 (1961).
16. Philippoff, W., "Viskosität der Kolloide," Edwards Brothers, Ann Arbor, Michigan (1943).
17. ———, *Trans. Soc. Rheol.*, **5**, 149 (1961).
18. ———, and F. H. Gaskins, *ibid.*, **2**, 263 (1958).
19. Roberts, J. E., "Proc. 2nd International Congress on Rheology," p. 91, Butterworth, London (1954).
20. Sakiadis, B. C., *A.I.Ch.E. Journal*, **8**, 317 (1962).
21. White, J. L., and A. B. Metzner, "Progress in Int. Research on Thermodynamic and Transport Properties," p. 748, Academic Press, New York (1962).

## The Influence of Operating and Static Liquid Holdups on Gas Absorption Rates in Chemically Reacting Systems

R. M. SECOR and R. W. SOUTHWORTH

Yale University, New Haven, Connecticut

An apparent anomaly which has been encountered repeatedly in packed tower studies of gas absorption with a rapid, irreversible chemical reaction is the observation of overall mass transfer coefficients which are far greater than the corresponding gas-phase mass transfer coefficients calculated from physical absorption data. Typically, the overall coefficient increases with increasing liquid-phase reactant concentration, eventually exceeding the physical absorption value of the gas-phase coefficient, frequently by a very considerable extent. Several investigators have shown that the overall coefficient becomes constant when the liquid-phase reactant concentration is increased sufficiently.

An explanation of these results was proposed by Shulman, Ullrich, and Wells (7) who visualized the interfacial area of the liquid in a packed tower to consist of the surfaces of both rapidly moving streams and quiescent

accumulations. In the case of physical absorption, the effective interfacial area is that of the rapidly flowing liquid. In the case of absorption with a rapid, irreversible chemical reaction, the presence of the liquid-phase reactant raises the absorptive capacity of the quiescent liquid. This liquid, even with its low rate of replacement, eventually becomes as effective as the rapidly moving streams at high concentrations of the liquid-phase reactant. Then the total interfacial area is effective for mass transfer. The principal experimental verification of this hypothesis is the following relation which has been demonstrated for packed tower operation (6):

$$\frac{(kga)_{r,v}}{(kga)} = C \frac{h_i}{h_o} \quad C \sim 1.0 \quad (1)$$

The sum of the static holdup,  $h_s$ , composed of the quiescent accumulations of liquid, and the operating holdup,  $h_o$ , composed of the rapidly flowing liquid, is equal to the total holdup of

liquid in the packing,  $h_t$ . All the holdups are expressed in units of liquid volume per unit packed volume. It has also been pointed out that for vaporization of liquids in packed towers, the entire liquid surface area should be effective for mass transfer (7). If the model is to be consistent, it must predict an eventual decrease in the gas-phase mass transfer coefficient when there is an increase in the rate at which the quiescent liquid approaches saturation, regardless of how this increase is accomplished. On this basis, Shulman, Ullrich and Wells (7) predicted for cases of absorption with a rapid, irreversible chemical reaction a decrease in the gas-phase mass transfer coefficient as the gas-phase solute concentration is increased. In descriptive terms, as the gas-phase solute concentration is decreased, the quiescent accumulations of liquid in the packing become increasingly effective for absorption since they require a longer time to become saturated. Also, an increase in the effective interfacial

R. M. Secor is with E. I. du Pont de Nemours and Company, Wilmington, Delaware.

## ABSTRACTS AND KEY WORDS

**Key Words:** A. Regression Analysis-8, Iterative-, Data-9, Experimental-1. B. Elimination-8, Computation-9, Normal-, Equations-9, Regression Analysis-10, Iterative-. C. Frequency-8, Convergence-9, Regression Analysis-10, Iterative-. D. Uses-8, Regression Analysis-9, Iterative-, Small-, Computers-10. E. Uses-8, Regression Analysis-9, Iterative-, Large-, Regressions-10. F. Solution-8, Simultaneous-, Equations-9, Iterative-, Regression Analysis-10.

**Abstract:** An iterative method for regression analysis is presented which does not require computation of the normal regression equations, is always convergent, and is applicable to large regressions even when computer memory is very limited. An example is given of the application of the method to experimental data, and the computational effort is compared with that of conventional direct methods. The method can also be applied to the solution of simultaneous equations.

**Reference:** Sommers, Roy W., Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 78 (1963).

**Key Words:** A. Simultaneous Differential Equations-8, Rate Constants-9, Nonlinear Regression-10, Concentration Time Data-1, Correlation Coefficients-9, Kinetic Model-8, Numerical Differentiation-10. B. Multicomponent Mixtures-1, Correlation Coefficient-9, Regression Coefficients-2, Lagrangian Multipliers-10, Quadratic Model-9. C. Bounded Regression Coefficients-2, Newton-Raphson Method-10.

**Abstract:** Conventional single-equation least squares regression techniques have gained widespread use in many industrial areas. A technique is presented here for the handling of systems of simultaneous regression equations. Examples are given of its application to the determination of a kinetic model, in studies of multicomponent mixtures, and in the estimation of regression coefficients having known bounds.

**Reference:** Dickinson, Allan W., Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 84 (1963).

**Key Words:** Nonlinear-1, Least Squares-8, Parameter-2, Estimation-2, Kinetics-8, Observations-1, Responses-1, Optimization-2, Digital Computer-10, Iteration-10.

**Abstract:** The numerical analysis and computational procedure of an iterative method for performing nonlinear least squares parameter estimation is described. The response function can be characterized explicitly or be contained as part of a system of differential equations. An example of the method applied to kinetic rate constant estimation is illustrated.

**Reference:** Rubin, Donald, Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 90 (1963).

**Key Words:** A. Computer-, Computations-8, Absorbers/Not Materials-9, Strippers-9, Redlich-Kister-, Equations-10. B. Nonideal-5, Multicomponent-5, Liquid Phase-5, Equilibrium-5, Trays-8.

**Abstract:** A computer program is described for a multicomponent absorber-stripper with heat balances on each tray and with nonideal vapor-liquid equilibria. These equilibria are computed using the multicomponent Redlich-Kister equations. Methods of avoiding convergence difficulties are discussed. Typical results are presented.

**Reference:** Davis, P. C., and B. A. Sobel, Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 95 (1963).

area would be expected. Since there were apparently no data available in the literature with which to test this prediction, it remained unverified. The results reported here were obtained in the course of a packed tower study of the absorption of ammonia from ammonia-air mixtures into aqueous solutions of boric acid. The following discussion is concerned with the effect of ammonia concentration in the gas on the mass transfer rate.

## APPARATUS AND PROCEDURE

The absorption tower consisted of a 6-in. I.D. Havg pipe packed with 20 in. of ½-in. carbon Raschig rings. The combined end effects were estimated to be the equivalent of an additional 4 in. of packing. The flow rates of the entering boric acid solution, entering air, and entering ammonia were determined with calibrated orifice meters. The ammonia concentration in the liquid leaving the column was determined by direct titration with standard hydrochloric acid, with methyl orange as the indicator (2). Boric acid itself is so weak that it has no appreciable influence on the hydrogen ion concentration, and the ammonia is titrated directly. Samples of the entering and leaving gas streams were analyzed for ammonia content by removing the ammonia in an absorption train and measuring the quantity of air passing through. The absorption train consisted of two vessels in series, each containing 4.0% boric acid solution, followed by one vessel containing phenolphthalein solution to reveal the presence of any unabsorbed ammonia. The absorbent solutions were analyzed for ammonia by the same procedure as that employed for the liquid leaving the absorption tower. In no case did the phenolphthalein indicate the presence of unabsorbed ammonia. The quantity of air associated with the ammonia was determined by permitting the air to displace the contents of a vessel initially filled with water. The volume of water collected equals the volume of air at the measured temperature and pressure in the vessel. Details of the operating procedure have been described elsewhere (3).

## EXPERIMENTAL RESULTS

A series of runs was carried out in which the liquid entering the column was a 4.00 weight percent solution of boric acid in water and the ammonia concentration in the entering gas was varied from 0.01 to 0.09 mole fraction. The gas and liquid rates were maintained constant at  $G = 400$  lb./hr. sq. ft. and  $L = 1,000$  lb./hr. sq. ft. The average of the terminal temperatures of each stream was kept close to 82°F. Although a temperature rise occurred in the liquid as a result of the chemical reaction, this did not influence the interpretation of the results, since the overall change in gas temperature was never greater than 4°F. As it has been

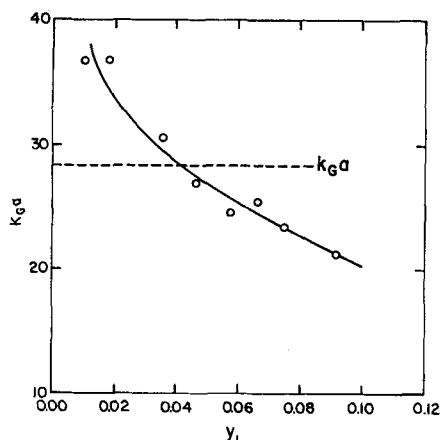


Fig. 1. Overall mass transfer coefficients for absorption of ammonia into 4% aqueous boric acid at  $G = 400$  lb./hr.sq.ft. and  $L = 1,000$  lb./hr. sq. ft.

shown that  $k_G$  varies approximately with the 0.09 power of the absolute temperature (3), the effect of temperature variations on the gas-phase mass transfer coefficient was well within the accuracy of the data. The average total pressure was maintained essentially constant at 795 mm. mercury.

The results are plotted in Figure 1. The value of  $k_G a$  shown on the ordinate was obtained from the experimentally determined  $K_G a$  for ammonia absorption in water (obtained in the same tower and under the same conditions as were the other data shown in Figure 1) and  $k_L a$  calculated from the correlation of Sherwood and Holloway (5). Equilibrium vapor pressures of ammonia over its aqueous solutions were calculated from an equation fitted to the data of Sherwood (4) and Breitenbach, the latter's results having been reported by others (1). The following results were obtained:

$$K_G a = 21.8 \text{ lb.-moles/hr. cu. ft. atm.}$$

$$k_L a = 26.1 \text{ lb.-moles/hr. cu. ft. (lb.-mole/cu. ft.)}$$

$$k_G a = 28.4 \text{ lb.-moles/hr. cu. ft. atm.}$$

Under the test conditions, the liquid phase resistance comprised about 23% of the total resistance to mass transfer. The overall mass transfer coefficients for absorption of ammonia in aqueous boric acid were calculated by dividing the mass transfer rate per unit packed volume by the logarithmic mean of the terminal driving forces. In calculating the logarithmic mean driving forces, it was assumed that the equilibrium vapor pressure of ammonia over the boric acid solutions was negligible. There is evidence to support this assumption for the conditions under which the value of  $K_G a$  exceeded  $k_G a$  (3). Although the assumption of zero vapor pressure of ammonia is convenient for expressing the experimental results in terms of mass transfer coeffi-

**Key Words:** Numerical Techniques-10, Slider Bearing-8, Hydrodynamic Lubrication-8, Partial Differential Equations-9, Computer Solutions-10, Lubricants Non-Newtonian-8.

**Abstract:** A numerical technique is developed for calculating the pressure distribution, flow pattern, load and frictional properties of a slider bearing operating hydrodynamically on a non-Newtonian lubricant. The calculation procedures which are developed are applicable to a class of nonlinear partial differential equations.

**Reference:** Steidler, F. E., and H. H. Horowitz, Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 99 (1963).

**Key Words:** Optimization-8, Experimenting-8, Evolution-8, Design-8, Maximum-8, Experiment-10, Processes-10, Correlations-10.

**Abstract:** This paper is an expository account of the ideas involved in determining the most efficient way to perform experiments on an operating chemical process, so that from such experiments, which involve only small deviations from normal, information is obtained about how well the process is currently functioning. Decisions can then be made in the direction of optimum performance. Some fundamental considerations in such strategy are discussed; mathematical formalism is held to a minimum.

**Reference:** Chanmugam, J., and G. M. Jenkins, Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 108 (1963).

## THERMODYNAMICS

Some thermodynamic properties of *n*-heptane, Doolittle, Arthur K., Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 1 (1963).

**Key Words:** Heptane-1, Internal Pressure-2, Coefficient of Thermal Expansion-2, Coefficient of Compressibility-2, Coefficient of Thermal Pressure-2, Thermal Pressure-2, Huddleston Equation-4, Cohesive Attraction-2, Specific Volume-1, Zero-Pressure Volume-1, Compressions-8, Pressure-Volume Data-8.

**Abstract:** The internal pressure of *n*-heptane has been calculated at temperatures from 0° to 300°C. and at pressures from 0 to 5,000 bars from published volumetric data. The coefficients of thermal expansion  $\alpha$ , compressibility  $B$ , and thermal pressure  $\gamma$  were calculated as prerequisites to the calculation of the internal pressure  $\pi$ . The accuracy of these calculated values varies with the temperature and pressure. The magnitude of the deviation decreases from several percent at 50 deg. and 100 bars to less than 0.1% at higher temperatures and pressures. A substantially linear relationship was observed between the logarithm of  $\gamma$  and specific volume  $v$ .

Partial molal volumes of hydrogen in liquid hydrocarbons, Connolly, J. F., and G. A. Kandalic, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 8.

**Key Words:** Partial Molal Volume-7, Hydrogen-8, Gas-8, Benzene-5, Octane-5, High Pressure-6, High Temperature-6, Dilatometric-10.

**Abstract:** The thermodynamic properties of a solute can be determined from vapor-liquid equilibrium data at high temperatures and pressures only if the partial molal volumes are known. Therefore, the densities of liquid mixtures of hydrogen in benzene and hydrogen in *n*-octane have been measured between 130° and 260°C. and up to 150 atm. Partial molal volumes of hydrogen in the concentration range 0 to 15 mol. percent hydrogen were derived from these data. The low-concentration partial molal volumes were checked with a dilatometric method.

Thermodynamic consistency tests for vapor-liquid equilibria data, Edmister, Wayne C., and Robert L. Robinson, Jr., Chem. Eng. Progr. Symposium Series No. 44, 59, p. 11 (1963).

**Key Words:** A. Vapor-Liquid Equilibrium-8, Consistency Tests-9, Review-. B. Activity Coefficient-10, Fugacity-10, K Values-10. C. Gibbs-Duhem-, Redlich-Kister-, Herington-, van Laar-, Margules-.

**Abstract:** A review of the theory and application of thermodynamic consistency tests for experimental vapor-liquid equilibrium data is presented. Rigorous relations for testing both isothermal and isobaric data are given. Several of the more widely used approximate consistency tests are discussed with emphasis on the assumptions required and limitations involved in their use. An attempt is made to verify and clarify the literature on this subject.

Thermodynamic properties of 2,2-dimethylpropane (neopentane), Heichelheim, H. R., and J. J. McKetta, Jr., Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 23 (1963).

**Key Words:** A. Properties-8, Thermodynamic-, 2,2-Dimethylpropane-8, Neopentane-8, Compressibility-9, Coefficients-9, Virial-, Second-, Fugacity-, Enthalpy-9, Entropy-9, Energy-9, Internal-, Free-, Differentiation-10, Integration-10, Graphical-. B. Apparatus-10, Burnett-, Modified-.

**Abstract:** A brief derivation is given of the expressions for deviation from ideal behavior of the thermodynamic functions of 2,2-dimethylpropane. From compressibility isotherms, cross plots are made to obtain isobars. The necessary partial derivatives are then obtained from these isobars and, together with functions of the compressibility isotherms, are used to calculate the deviations from ideality. The curves involved also conveniently give second virial coefficients. All differentiation and integration is done graphically. The compressibility data were obtained with a modified Burnett apparatus.

Condensed phase diagram of the system argon-nitrogen, Long, H. M., and F. S. DiPaolo, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 30 (1963).

**Key Words:** Liquid-1, Solid-2, Phase Diagram-8, Argon-9, Nitrogen-9, Heating-10, Cooling-10, Freezing-10, Calorimeter-10, Vapor Pressure-7, Polarized Light-5, Temperature-5, Composition-6, Liquidus Line-7, Solidus Line-7, Crystallization-7, Crystal Structure-7, Azeotrope-8, Birefringence-8, Peritectic-8, Miscibility-8, Cubic-, Hexagonal-, Condensed-, Low-, Glass-.

**Abstract:** A determination of the condensed phase diagram of the argon-nitrogen system by thermal analysis has indicated the existence of a thermal halt of the peritectic type. Optical examination of the solids formed from argon-nitrogen mixtures has demonstrated the change in structure expected for a peritectic system. Experimental values of vapor pressure and liquidus and solidus points are given.

Liquid-vapor equilibrium compositions of carbon dioxide-oxygen-nitrogen mixtures, Zenner, G. H., and L. I. Dana, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 36 (1963).

**Key Words:** Carbon Dioxide-1, Oxygen-1, Nitrogen-1, Liquid-4, Vapor-4, Equilibrium-8, Phase Equilibria-8, Mixture-2, Binary Mixture-2, Ternary Mixture-2, Solubility-2, Solution-2, Gas Mixture-8, Pressure-4, Temperature-4, Critical Pressure-8, Critical Temperature-8, Tables-8, Composition-8, Vapor Pressure Enhancement-8.

**Abstract:** Liquid-gas phase equilibrium compositions for the systems carbon dioxide-oxygen, carbon dioxide-nitrogen, and carbon dioxide-oxygen-nitrogen were measured from  $-55^{\circ}\text{C.}$  to  $0^{\circ}\text{C.}$  and at various pressures up to 145 atm. Data are given in tables and are plotted on curves. The vapor phase enhancement of carbon dioxide is evident as is also the solubility of oxygen and nitrogen in carbon dioxide liquid. Although oxygen is roughly 50% more soluble in liquid carbon dioxide than nitrogen, in the ternary mixtures the ratio of oxygen to nitrogen in the liquid phase is very close to that in the gas phase.

Coefficient of thermal expansion: reduced state correlation for the gaseous and liquid states of pure substances having simple molecular structure, Damasius, Gediminas, and George Thodos, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 42 (1963).

**Key Words:** Coefficient of Thermal Expansion-8, Natural Convection-6, Reduced State Correlation-8, Argon-9, Krypton-9, Xenon-9, Nitrogen-9, Oxygen-9, Carbon Monoxide-9, Methane-9, Gases-9, Liquids-9, Fluids-9, Physical Properties-8.

**Abstract:** A reduced state correlation for the coefficient of thermal expansion of pure substances having simple molecular structure has been developed from PVT data available in the literature for argon. The coefficient of thermal expansion was expressed in terms of reduced variables and a reduced state density correlation was developed for argon. This density correlation was then utilized to develop plots of the dimensionless variable  $\beta T_c$  against  $T_R$  and  $P_R$  for reduced temperatures up to  $T_R = 3.0$  and reduced pressures up to  $P_R = 50$ .

cients, the conclusions to be formed are independent of it. The salient result demonstrated by Figure 1 is that the overall mass transfer coefficient increases with decreasing ammonia concentration in the gas and eventually exceeds the physical-absorption value of  $k_{ga}$  when the mole fraction of ammonia in the entering gas drops below about 0.042.

Figure 2 shows the effect of the entering gas composition on the leaving gas composition (no assumptions having been made regarding the equilibrium vapor pressure of ammonia over boric acid solutions). The dashed line is a plot of the equation

$$\frac{y_2}{y_1} = e^{-\frac{k_{oah}P}{G_M}} \quad (2)$$

which is the relation for physical absorption in the absence of liquid-phase resistance for dilute gases. For the experimental conditions, the exponent in Equation (2) is  $-4.3$ . The fact that the experimental data plotted in Figure 2 fall considerably below the dashed line at low ammonia concentrations is consistent with the proposal of a higher effective interfacial area for absorption with chemical reaction than for physical absorption.

It is of interest to calculate the expected maximum value of the gas-phase mass transfer coefficient, that is, that which would be obtained if the effective interfacial area were equal to the total interfacial area. Substituting the appropriate values of the holdups (7) and the proportionality constant (6) into Equation (1) gives

$$(k_{ga})_{r,v} = \frac{(0.95)(0.068)(28.4)}{(0.0355)} =$$

$$51.7 \text{ lb.-moles/hr. cu. ft. atm.}$$

It is seen that this value has not yet been reached even at the lowest ammonia concentration employed.

It is concluded that the experimental results are entirely consistent with the model of packed tower operation described (6) and verify the predicted effect of gas-phase solute concentration. The model, in its present form, cannot predict quantitatively the effect of gas-phase solute concentration on the mass transfer rate for absorption with chemical reaction in a packed tower, although it does predict the maximum rate attainable. The experimental verification of the qualitative aspects of the model does, however, provide a firmer basis for the physical representation proposed. This representation, based on the varying absorptive capacity of quiescent accumulations of liquid in the packing, accounts for the previously unexplained effect of liquid-phase reactant concen-

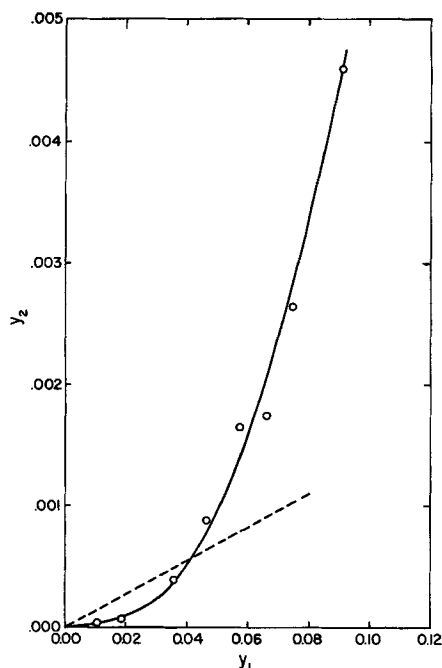


Fig. 2. Effect of entering gas composition on leaving gas composition for absorption of ammonia into 4% aqueous boric acid at  $G = 400$  lb./hr. sq. ft. and  $L = 1,000$  lb./hr. sq. ft. The dashed line is the relation for physical absorption in the absence of liquid-phase resistance.

tration on the mass transfer rate for absorption with chemical reaction.

#### LITERATURE CITED

1. Kowalke, O. L., O. A. Hougen, and K. M. Watson, *Bull. University of Wisconsin Expt. Sta. Ser. No. 68* (1925).
2. Scott, W. W., "Standard Methods of Chemical Analysis," Vol. 1, D. Van Nostrand, New York (1922).
3. Secor, R. M., D. Eng. thesis, Yale University, New Haven, Connecticut (1958).
4. Sherwood, T. K., *Ind. Eng. Chem.*, **17**, 745 (1925).
5. ———, and F. A. L. Holloway, *Trans. Amer. Inst. Chem. Engrs.*, **36**, 21 (1940).
6. Shulman, H. L., C. G. Savini, and R. V. Edwin, *A.I.Ch.E. Journal*, **9**, 479 (1963).
7. Shulman, H. L., C. F. Ullrich, and N. Wells, *ibid.*, **1**, 247 (1955).

#### NOTATION

- $a$  = effective interfacial area, sq. ft./cu. ft.  
 $C$  = a constant  
 $G$  = average superficial gas rate, lb./hr. sq. ft.  
 $G_M$  = average superficial molal gas rate, lb.-moles/hr. sq. ft.  
 $h$  = tower height, ft.  
 $h_o$  = operating holdup, cu. ft./cu. ft.  
 $h_s$  = static holdup, cu. ft./cu. ft.  
 $h_t$  = total holdup, cu. ft./cu. ft.

Phase relations of binary systems that form azeotropes: *n*-alkanes-perfluoro-*n*-heptane systems (ethane through *n*-nonane), Jordan, Lawrence W., Jr., and Webster B. Kay, *Chem. Eng. Progr. Symposium Ser. No. 44*, 59, p. 46 (1963).

**Key Words:** Phase Behavior-8, Phase Patterns-8, Binary Systems-8, Azeotropes-8, Physical Properties-8, Critical Locus-8, Critical Temperature-8, Critical Pressure-8, Critical Volume-8, Perfluoro-*n*-Heptane-8, *n*-Paraffins (Ethane to *n*-Nonane)-8, Correlations-8.

**Abstract:** The phase behavior in the critical region of binary systems composed of perfluoro-*n*-heptane with the normal alkanes, ethane through nonane, was studied. Minimum temperature points in the critical locus curves indicating the formation of positive azeotropes were found for the systems from *n*-butane through *n*-octane. The propane system showed a temperature plateau between the critical temperatures of the pure components. The ethane and nonane systems exhibited the normal maximum pressure type of critical locus curves without maximum or minimum points in temperature. The results show that systems which form azeotropes in the critical region are characterized by a pattern of phase behavior distinctly different from that for nonazeotropic systems.

Measurement of the thermodynamic properties of gases at low temperature and high pressure-methane, Jones, M. L., Jr., D. T. Mage, R. C. Faulkner, Jr., and D. L. Katz, *Chem. Eng. Progr. Symposium Ser. No. 44*, 59, p. 52 (1963).

**Key Words:** Methane-5, Temperature-6, Pressure-6, Composition-6, Enthalpy-7, Isobaric Specific Heat-7, Specific Heat at Constant Pressure-7, Integral Latent Heat of Vaporization-7, Specific Heat at Constant Pressure-8, Calorimeter-8, Design-8, Measurement-8, Instrumentation-8, Construction-8, Drawing-8, Methane-8, Methane, Enthalpy-9, Methane, Integral Latent Heat of Vaporization-9, Methane, Specific Heat at Constant Pressure-9, Methane Pressure-Enthalpy-Temperature Chart-9, Calorimeter-10, Methane-10, Katz-, Jones-, Mage-, Faulkner-, University of Michigan-, Michigan-.

**Abstract:** A flow calorimeter system has been designed and constructed which is capable of measuring isobaric heat capacities and latent heats of vaporization of light gases and their mixtures at temperatures from  $50^\circ$  to  $-250^\circ$  F., and at pressures from 150 to 2,000 lb./sq. in. abs. Measurements were made on methane in this region and used, along with selected properties from the literature, to construct a pressure-enthalpy-temperature chart.

Experimental enthalpies for nitrogen, Mage, David T., Millard L. Jones, Jr., Donald L. Katz, and John R. Roebuck, *Chem. Eng. Progr. Symposium Ser. No. 44*, 59, p. 61 (1963).

**Key Words:** A. Specific Heat-8, Latent Heat-8, Nitrogen-8, Flow Calorimeter-10, Measurement-8, Pressure-6, Temperature-7. B. Joule-Thomson Coefficient-9, Measurement-10. C. Pressure-Enthalpy Diagram-8, Temperature-7.

**Abstract:** A flow calorimeter has been used to measure the latent heat and specific heat at constant pressure of nitrogen. These values have been combined with previous measurements of Joule-Thomson coefficient to construct a pressure-enthalpy-temperature diagram. The range of the diagram is from  $-320^\circ$  to  $+50^\circ$  F., and from 0 to 3,000 lb./sq. in. abs.

Solubility of sulfur dioxide in polar organic solvents, Albright, Lyle F., Paul T. Shannon, Sun-Nien Yu, and Ping Lin Chueh, *Chem. Eng. Progr. Symposium Ser. No. 44*, 59, p. 66 (1963).

**Key Words:** Solubility-8, Correlation-8, Complex Formation-8, Heat of Mixing-8, Sulfur Dioxide-1, Tetraethylene Glycol Dimethyl Ether-1, N,N-Dimethylacetamide-1, N,N-Dimethylformamide-1, 2-Octanone-1, Ethyl Laurate-1, Nitrobenzene-1, *n*-Heptyl Alcohol-1, Solutions-2, Temperature-6, Composition-6, Pressure-7, Heat of Mixing-7, Functionality-7.

**Abstract:** The solubility of sulfur dioxide in polar organic solvents probably results from complexes being formed between the positive sulfur atom in sulfur dioxide and the electronegative polar group of the solvent. The solubility characteristics of sulfur dioxide in polar solvents are very similar to those of chlorofluoromethanes containing a hydrogen atom. Three solvents, tetraethylene glycol dimethyl ether (best on mole basis), dimethylacetamide and dimethylformamide (best on weight basis) are excellent solvents for sulfur dioxide.

Analysis of the data in terms of activities and activity coefficients based on a modification of the approach of Mastrangelo was found to be a good method for correlating the data even though the same correlating equation was shown to result from different mathematical models. Heats of mixings calculated from the solubility data were found to be maximum at a mole ratio of solute to solvent very close to the functionality values of the solvents.

## ABSTRACTS AND KEY WORDS

Methods of estimating the thermodynamic properties of halogenated ethylene compounds, Beckwith, William F., and Raymond W. Fahien, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 75 (1963).

**Key Words:** Property, Thermodynamic-2, Entropy-2, Heat Capacity-2, Normal Boiling Point-2, Statistical Mechanics-4, Group Contribution Method-8, Tetraiodoethylene-9, Halogenated Ethylenes-9, Wave Numbers-1, Interatomic Distances-1.

**Abstract:** A group contribution method was devised to estimate the ideal gas thermodynamic properties of halogenated ethylene compounds. The method, which is based on the statistical mechanical equations, divides the total property into contributions due to translation motion, vibrational motion, and external rotational motion. The method was used to predict the properties of tetraiodoethylene. Values of entropy, heat capacity, critical properties, normal boiling point, interatomic distance, and wave numbers for the halogenated ethylene compounds are tabulated.

The specific heat of a natural gas and methane at 69 and 103 atmospheres, Hujak, K. C., H. R. Froning, and C. S. Goddin, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 88 (1963).

**Key Words:** Natural Gas-1, Methane-1, Specific Heat-8, Pressure-6, Temperature-6, Calorimeter-10, Prediction-9, Extrapolation-9.

**Abstract:** Specific heats at constant pressure ( $C_p$ ) of a natural gas and pure methane were measured at 69 and 103 atm. at temperatures between  $-20^\circ$  and  $80^\circ\text{F}$ . in a flow calorimeter. Several prediction methods based on PVT relationships and an equation of state were found to reliably predict specific heats of these gases at these conditions. Published extrapolations of experimental data were found to contain large errors.

Thermodynamics of solutions: VIII. An improved equation of state, Redlich, Otto, and A. K. Dunlop, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 95 (1963).

**Key Words:** Equation of State-1, Compressibility Factor-1, Fugacity-1, Fugacity Coefficient-1, Gaseous Mixtures-1, IBM 7090-10, Computer-10, Thermodynamics-1.

**Abstract:** An improvement of the equation of state of Redlich and Kwong furnishes the compressibility factor, fugacity, and fugacity coefficient(s) for single components or gas mixtures. Required data are the temperature, pressure, and composition in addition to the critical temperature and pressure and the acentric factor  $\omega$  of Pitzer et al for each of the components. Use of an IBM-7090 for the calculations is desirable.

Vapor-liquid equilibrium in the helium-nitrogen system, Buzyna, George, Robert A. Macriss, and Rex T. Ellington, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 101 (1963).

**Key Words:** A. Natural Gas-1, Helium-2, Nitrogen-3, Cryogenic-5, Phase Equilibrium-6, Distillation-7, Design-8, Column-10. B. Natural Gas-1, Helium-2, Nitrogen-3, Cryogenic-5, Temperature-6, Pressure-5, Phase Composition-7, Thermodynamics-8, Phase Apparatus-9, Phase Apparatus-10.

**Abstract:** Helium is recovered from natural gas using phase equilibrium behavior at cryogenic temperatures. Experimental vapor-liquid equilibrium data for the helium-nitrogen system are given for  $-233^\circ$  to  $-320^\circ\text{F}$ . and 170 to 1,000 lb./sq. in. abs. Disagreements in literature data are reconciled. Significant detail is added to liquid-phase information important to cycle design regarding helium lost in waste nitrogen separator bottoms.

The integral isobaric heat of vaporization of mixtures, Stein, Fred P., and Joseph J. Martin, Chem. Eng. Progr. Symposium Ser. No. 44, 59, p. 112 (1963).

**Key Words:** Heat of Vaporization-8, Latent Heat-8, Integral Isobaric-8, Isopropyl Alcohol-8, Water-8, Acetone-8, Latent Heat Equation-10, Enthalpy-8, Binary Mixtures-8.

**Abstract:** The integral isobaric heats of vaporization of the isopropyl alcohol-water system and the acetone-water system have been measured in an adiabatic flow calorimeter at atmospheric pressure. The data obtained have been used to construct accurate enthalpy-concentration diagrams for the systems studied and to serve as the criteria for evaluating methods of predicting integral isobaric heats of vaporization. An equation has been developed which relates the integral isobaric heat of vaporization to the heat of vaporization of the pure components at the bubble-point temperature of the mixture, the ideal-gas specific heats of the pure component, and the bubble-and-dew-point temperatures of the mixture.

$k_{Ga}$  = gas-phase mass transfer coefficient for physical absorption, lb.-moles/hr. cu. ft. atm.

$(k_{Ga})_{r,v}$  = gas-phase mass transfer coefficient for absorption with a rapid chemical reaction at high liquid-phase reactant concentrations or for vaporization, lb.-moles/hr. cu. ft. atm.

$K_{Ga}$  = overall mass transfer coefficient, lb.-moles/hr. cu. ft. atm.

$k_{La}$  = liquid-phase mass transfer coefficient for physical absorption, lb.-moles/hr. cu. ft. (lb.-mole/cu. ft.)

$L$  = average superficial liquid rate, lb./hr. sq. ft.

$P$  = total pressure, atm.

$y_1$  = mole fraction of solute in entering gas

$y_2$  = mole fraction of solute in leaving gas

## ERRATA

The ordinate scale (hydrogen sulfide capacity) in Figure 7 of the article "Adsorption of Normal Paraffins and Sulfur Compounds on Activated Carbon" by R. J. Grant, Milton Manes, and S. B. Smith, which appeared on page 403 of the July, 1962, issue of the *A.I.Ch.E. Journal* should be multiplied by a factor of ten.

In Equation (12) of the article "Mass Transfer and Effective Interfacial Areas in Packed Columns" by Fumitake Yoshida and Tetsushi Koyanagi, which appeared on page 309 of the July, 1962, issue of the *A.I.Ch.E. Journal*,

$\left(\frac{\mu_L}{\rho_L D_L}\right)^{1/2}$  is missing before

$$\left(\frac{d_p^3 g \rho_L^2}{\mu_L^2}\right)^{-1/6}$$

The captions for Figures 1 and 2 of the article "The Rate of Glycerol Absorption by Ion Exchange Resins" by Richard P. Griffin and J. S. Dranoff, which appeared on page 283 of the March, 1963, issue of the *A.I.Ch.E. Journal*, should read as follows: Figure 1. Correlation of data from elution experiments; Figure 2. Correlation of data from saturation experiments.