Isobaric Equilibrium Calculations

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Dodge and Ibl (*3*) have pointed out that the thermodynamic consistency criterion proposed by Redlich and Kister (*6*) should have the following form for the case of variable temperature and constant pressure conditions:

$$\int_0^1 \ln(\gamma_1/\gamma_2)\,dx_1 = \int_0^1 -Z_1\,dx_1 \qquad (1)$$

where

$$Z = -\Delta H/RT^2\,(dT/dx_1)_p$$

and

$$\Delta H = H - x_1H^o{}_1 - x_2H^o{}_2$$

Where the enthalpy term is not negligible, the equal area thermodynamic consistency check of Redlich and Kister does not apply. As there is no way of predicting when the Z term may be neglected a priori, its existence can be determined only by drawing the γ-ratio vs. composition graph and checking the area values. There is, therefore, no justification for adjusting this curve for isobaric systems to give equal areas.

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Apparent Inert-Gas Permeation Through Nickel

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For some time it has been considered a fact that the inert gases do not permeate metals (*5*). This has been attributed to the fact that the gas atoms are not adsorbed on the surface of the metal, and do not penetrate into the metal lattice (*4*). However, at various times observations have been made which appear to contradict the fact that inert gases do not permeate. For example, at elevated temperatures, gas has been observed to accumulate in an evacuated stainless steel cylinder even though it was surrounded by argon (*3*, *6*). Harden (*3*) studied the argon-nickel system and his results, though incomplete, indicated that some form of gas-metal permeation occurred. The present study was made to explain the above results and to examine the statement "no rare gas permeates any metal (*5*)."

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TABLE 1. MASS SPECTROMETER ANALYSIS

	Composition mole %					
Sample	H_2	He	H_2O	N_2	O_2	A
Permeated gas (A-5)	79	0	6	11	3	1
Permeated gas (A-6)	10	0	39	40	10	1
Delivered gas (A-5, A-6)	0	98.9	0.4	0.6	0.1	0

TABLE 2. EXPERIMENTAL RESULTS

Run*	Gas	Temperature, °C.	Pressure, lb./sq.in.abs.	Equilibrium pressure, mm. Hg
A-1	He	793	731	3.8
A-2†	He	793	362	0.015
A-3	He	797	529	0.041
A-4	He	803	702	0.036
A-5	He	804	800	0.085
A-6	He	802	782	0.018
B-1	A	798	597	0.465
B-2†	A	782	584	0.014
B-3	A	793	584	0.108
Ref. 3	A	907	1,475	~2.94
Ref. 3	A	806	1,415	~1.9

* Run sequence was A-1 through A-4, B-1 through B-3, A-5 and A-6.
† Questionable whether permeation was detected.

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Several investigations (*4, 6, 8*) lend some support to the view that inert gases do permeate metals. Le Claire and Rowe (*4*) showed that argon will diffuse through a silver lattice following introduction of argon by ion bombardment. Van Wieringer and Warmoltz (*7*) studied permeation of hydrogen and helium through the semiconductors, silicon, and germanium. They found helium would permeate these materials at a rate of about 4×10^{-4} of that for hydrogen. Furthermore, the permeation of hydrogen was found to be dependent on the square root of the pressure as in true metals, indicating dissociation to atoms. Other investigators (*8*) have reported the penetration of steel by helium when working with high pressure at low temperature.

EXPERIMENTAL SYSTEMS AND APPARATUS

Systems

Two gas-metal systems were studied. They were argon-nickel and helium-nickel. Specially purified argon was used which contained maximum impurities of 3 parts/million each of nitrogen, oxygen, and water, 1 part/million of hydrogen, and 1 part/million (total) for all others. The helium was specified to be 99.99% pure.

Apparatus

The permeation membrane [a detailed description of which is available (*3*)] was made of pure vacuum-cast nickel. Basically, it was a hollow cylinder 20.638 cm. long, 0.9525 cm. thick, with an I.D. of 1.27 cm. One end was a hollow hemisphere with the same thickness as the cylinder.

The membrane was enclosed in a cylindrical stainless steel jacket. A welded seal joined the membrane to the jacket at the gas delivery end. The space between the membrane and jacket served as part of the gas-collecting system.

The equipment was the same as Phillips and Dodge used in their study of hydrogen permeation through stainless steel (*6*). Certain significant aspects of this equipment will be mentioned briefly here and in the next section. [Although modified in many respects, this equipment is also the same as that described in detail by Bryan (*1*).]

The permeation membrane was heated by an electric tube furnace. Appropriate tubing provided cold connections to the high-pressure (gas-delivery) and vacuum (gas-collecting) systems. Temperature was measured by four chromel-alumel thermocouples, and a 5,000 lb./sq.in. Heise gauge measured gas-delivery pressures.

EXPERIMENTAL PROCEDURE

To begin an experimental run, helium or argon was introduced to the inside of the nickel membrane. Permeation took place outward through the membrane wall and into the surrounding evacuated

INFORMATION RETRIEVAL*

The study of gas-solid equilibrium at high pressures by gas chromatography: Part I. Ethane, propane, and *n*-butane at essentially infinite dilutions in the methane-silica gel system, Gilmer, H. B., and Riki Kobayashi, **A.I.Ch.E. Journal, 10,** No. 6, p. 797 (November, 1964).

Key Words: A. Equilibrium-8, Gas-1, Solid-5, Methane-1, Ethane-1, Propane-1, *n*-Butane-1, Silica Gel-5, High Pressure-5, Chromatography-10, Ethylene-1, Adsorption-2, Thermodynamics-7. B. Analysis-8, Composition-8, Chromatography-10, Gas-1, *n*-Hydrocarbon-1, Methane-6, Ethane-7, Propane-7, *n*-Butane-7. C. Apparatus-10, Fixtures-8, Valves-8, Neoprene-10, High Pressure-5.

Abstract: An equation for determining the *K* values or the ratio of the concentration of a component in the gas phase to that in the adsorbed phase at essentially infinite dilutions has been developed and applied to obtain ***K*** values at essentially infinite dilution concentrations of ethane, propane, and *n*-butane in the methane-silica gel system. The heats of adsorption for the same solutes at essentially infinite dilutions have been obtained. Studies were conducted from —40° to +40°C. up to a maximum pressure of 2,000 lb./sq.in.abs.

Diffusion and flow in a radially moving film, Merson, R. L., and J. A. Quinn, **A.I.Ch.E. Journal, 10,** No. 6, p. 804 (November, 1964).

Key Words: Liquid-Liquid Interface-8, Mass Transfer-8, Diffusion-6, Isobutanol-9, Ethyl Acetate-9, Water-5, Contact Time-8, Interfacial Turbulence-8, Velocity Profile-6, Stagnation-9, Interfacial Tension-6.

Abstract: Diffusion through a planar liquid-liquid interface has been studied with several binary systems. A thin film of water flowing radially outward from a central source was contacted with a variety of pure organic liquids and also with carbon dioxide. The measured rates of mass transfer can be predicted exactly by using the true surface age in the standard diffusion calculations. The interface was visible at all points, allowing direct measurement of surface ages between 1 and 50 sec. Gradual stagnation of the interface due to ever-present trace quantities of surface-active impurities was observed for systems of high interfacial tension.

The behavior of immiscible liquids in concurrent flow through packed beds, Rigg, Robert G., and Stuart W. Churchill, **A.I.Ch.E. Journal, 10,** No. 6, p. 810 (November, 1964).

Key Words: Concurrent-8, Columns-5, Density-6, Dispersing-8, Droplets-7, Extraction-9, Fluid Flow-8, Holdup-7, Immiscible-5, Interfacial Tension-6, Isobutanol-5, Isooctane-5, Liquids-5, Packings-5, Porosity-6, Pressure Gradient-7, Reynolds Number-6, Sauter Mean-7, Slip Velocity-9, Spheres-5, Surfactant-4, Viscosity-6, Water-5, Weber Number-6.

Abstract: Pairs of immiscible fluids were pumped concurrently upward through beds of glass spheres. The pressure gradient was found to go through a maximum as the flow of one fluid increased with a constant flow of the other fluid. A general correlation for the pressure gradient was developed in terms of the Weber number, but the pressure gradient was unaffected by the addition of a surfactant. In transient experiments the initial phase holdup was found to decay exponentially. The droplet diameters were found to have a Gaussian distribution. A generalized correlation was developed for the Sauter mean droplet diameter.

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* For details on the use of these Key Words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr.,** Vol. 60, No. 8, p. 88 (August, 1964). A free copy of this article may be obtained by sending a post card, with the words "Key Word Article" and your name and address (please print) to Publications Department, A.I.Ch.E., 345 East 47 St., N.Y. N.Y., 10017. Price quotations for volume quantities on request.

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space. Permeation rates were determined by collecting the permeated gas in a known volume and measuring the resulting pressure rise. The ideal gas law was then used to compute the rate. Pressure in this section was measured with a modified three-scale McLeod type of vacuum gauge.

A mercury diffusion pump controlled pressure at the exit surface of the membrane. When the pump was running, the permeated gas was pumped quickly away from the membrane surface and into a static collecting volume. This resulted in a negligible back pressure (about 1μ) on the membrane. However, one could allow a back pressure to build up by not using this pump. The permeation rate could be determined in either case.

When the membrane was above room temperature, an argon purge was maintained in the furnace core. This served both as a safety precaution and to minimize permeation of gas into the collecting system through the permeation assembly jacket and connecting tubing. Despite this precaution, blank accumulation (believed to be the result of gas permeating through the jacket wall) was observed at high temperatures. This phenomenon has been discussed in detail (*6*) and, in part, suggested the present study.

To prevent misinterpretation of permeation results, Norton (*5*) has stated the following: "(1) There should be available analytical means of measuring and identifying the very small amount of gas diffusing through. The mass spectrometer is ideal for this purpose. . . . (2) The degassing of the metal should be very thorough so the blank gas evolution can be low. (3) The specific gas studied must be identified coming through after that gas has been applied to the high pressure side. . . ." The present study satisfied these criteria as discussed below.

Between runs, the permeation membrane was completely degassed (normally for about 20 hr.) at the operating temperature. A blank run (vacuum on the high pressure side) of 2 to 3 hr. was made just before each run. This was to test for possible leaks or gas evolution and to measure blank accumulation rates. (No accumulation or leakage was detected in two tests made at room temperature.)

Samples of the permeated gas were taken from the gas-collecting systems during Runs A-5 and A-6 and analyzed with a mass spectrometer. A sample of helium taken from the delivery system during these runs was similarly analyzed. The results are presented in Table 1.

EXPERIMENTAL RESULTS

Figure 1 presents a picture typical of the experimental results. It is a plot of pressure in the gas-collecting system as a function of time for Run A-5. At time zero, helium was delivered at 800 lb./sq.in.abs. to the previously degassed membrane with the mercury diffusion pump not operating. For the first half hour, pressure built up in a

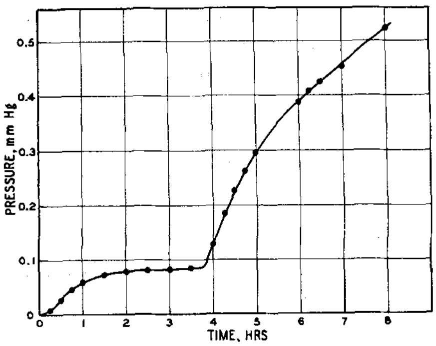

Fig. 1. Collecting system pressure vs. time. Run A-5, helium-nickel system.

manner typical of unsteady state permeation. However, the rise of pressure with time failed to show the linear relation characteristics of steady state permeation. Instead, the rate of pressure buildup decreased until a characteristic equilibrium pressure was reached after which permeation apparently stopped.

After the equilibrium pressure was established, at about 4 hr. the diffusion pump was turned on. (From this point on there was a negligible back pressure on the exit surface of the permeation membrane.) Pressure in the collecting system (output side of the pump) began to rise immediately, and soon a relatively constant rate of pressure rise was observed. This was because of a resumption of permeation. However, over the last 4 hr. of the run there was a tendency for the permeation rate to fall slightly. Similar results were obtained in the runs with argon.

Table 2 presents the results of this study. Nine runs were made at high temperature. In seven of these runs, permeation was definitely detected. True or observed values of equilibrium pressure are reported in Table 2. Usually, blank accumulation would account for less than 20% of the observed pressure value.

The phenomenon of equilibrium pressure (permeation stopping) is believed to result from a balanced permeation driving force across the membrane. Thus, assuming no actual leaks, the equilibrium pressure is identical to the effective partial pressure of the permeating gas. This explanation accounts for the behavior of runs such as A-5 (Figure 1). On the other hand, the possibility that permeation stopped due primarily to depletion of the permeating gas at the entrance surface and/or to buildup of a permeation barrier at either membrane surface is inconsistent with the behavior of Run A-5. In addition, after equilibrium pressure was reached in Run A-1, helium on the high pressure side was replaced with fresh helium at the original pressure.

INFORMATION RETRIEVAL

(*Continued from page 970*)

Two-phase, annular, laminar flow of simple fluids through cylindrical tubes, Slattery, John C., **A.I.Ch.E. Journal, 10,** No. 6, p. 817 (November, 1964).

Key Words: Two-Phase Flow-8, Simple Fluid-8, Pressure Drop-9, Volume Rate of Flow-9, Tube-, Pipe-, Viscoelastic-, Non-Newtonian-, Coleman-, Noll-, Surface Tension-.

Abstract: The relationship between volume flow rate and the driving force per unit length of pipe is obtained for two simple fluids of Noll in two-phase, annular, laminar flow through a very long cylindrical tube. In order that the flow be annular either the densities of the two phases must be very nearly the same or gravity must act along the axis of the tube.

The mechanics of vertical gas-liquid fluidized systems I: countercurrent flow, Bridge, A. G., Leon Lapidus, and J. C. Elgin, **A.I.Ch.E. Journal, 10,** No. 6, p. 819 (November, 1964).

Key Words: Air Bubbles-1, Liquid-1, Generalized Rigid Particle Theory-1, Fluidized System-2, Slip Velocity Ratio-6, Holdup-6, Flooding-8, Mass Transfer-8, Contacting-10.

Abstract: The generalized theory of fluidized system developed in these laboratories has been shown experimentally to be valid for the case of small air bubbles rising countercurrently through a variety of liquids. The results showed that if the column were not in a flooded state, the relationship between the slip velocity ratio and the holdup for each system was independent of the system parameter, and this relationship was identical with that expected for the analogous, particulately fluidized bed of rigid particles. Two types of flooding phenomena were observed. These have tentatively been named ***dispersed-phase flooding*** and ***continuous-phase flooding,*** respectively, because of their general nature. The latter can be predicted from the generalized theory, but the former appears at lower flow rates than theoretically predicted.

Droplet characteristics in a countercurrent contactor, Olney, R. B., **A.I.Ch.E. Journal, 10,** No. 6, p. 827 (November, 1964).

Key Words: Liquid Extraction-8, Countercurrent-10, Rotating Disks-10, Equilibrated Phases-5, Drop Size-8, Rise Velocity-8, Contact Time-8, Size Distribution Parameters-9, Eddy Diffusion-8, Residence Time Distribution-9, Joint Distribution-9, Mass Transfer-8, Uniform Drop Model-9, Drop Swarm Model-9.

Abstract: Drop size distributions have been determined for several liquid pairs in a rotating disk contactor. These data are analyzed in terms of mean diameter dynamics, an upper limit—lower limit size distribution, and a joint distribution of drop rise times plus eddy diffusion. The problem of interpreting mass transfer—eddy diffusion processes for a drop population in terms of a uniform drop model is discussed, and the appropriate integral model for a drop swarm is presented.

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The equilibrium pressure was not affected, which is additional evidence against the consideration of gas depletion.

DISCUSSION OF RESULTS

Permeation of gas through the nickel membrane was definitely detected in seven of the nine runs made. However, neither helium nor argon permeated through nickel in these experiments. Three pieces of evidence support this conclusion. First, no helium could be detected in the samples of permeated gas obtained from Runs A-5 and A-6. Second, permeation was not observed in every run. Third, if the inert gases were permeating, there would be no ready explanation of the equilibrium pressure.

The surprising aspect of these experiments [and two conducted by Harden (3)] is that permeation was observed at all. Once permeation was detected, however, it was natural to suspect that the permeating gas was hydrogen. Hydrogen has extremely high permeation rates relative to other gases and readily permeates most metals.

The results presented in Table 1 show that a significant portion of the samples of permeated gas taken from Runs A-5 and A-6 was hydrogen. The fact that 100% hydrogen was not found is best explained by difficulties encountered in obtaining and analyzing the samples. Thus, it is not surprising that oxygen, nitrogen, and water vapor should be present, as these are common contaminants. However, the presence of hydrogen is significant, as it is not a contaminant which could be introduced because of experimental technique.

Other findings support the belief that hydrogen was the permeating gas. In Run A-1, steady state permeation was observed for a relatively long period of time. This permitted the time lag for the run to be determined with a fair degree of accuracy. From the time lag, the diffusivity of the permeating gas in nickel was calculated, by the method of Daynes (2), to be 1.21×10^{-4} sq. cm./sec. Harden (3) reports the diffusivity of hydrogen in nickel, at approximately the same temperature, to be 1.02×10^{-4} sq.cm./sec. In addition, a calculation was made of the hydrogen permeation rate corresponding to the relatively constant rate of pressure rise over the last 2 hr. of Run A-5 (Figure 1). From this rate and Harden's (3) data on the permeation of hydrogen through nickel, an effective hydrogen partial pressure of 0.052 mm. of mercury was calculated. This compares to a measured value of 0.085 mm. of mercury for the run.

Water vapor is believed to be the hydrogen source. It is unlikely that the water vapor was originally present in the inert gases but might have been introduced by faulty experimental technique (that is, saturated gas drying bed). In any event, our analysis of the gas taken from the delivery system (98.9% helium) differs from the specified purity (99.99% helium).

From equilibrium calculations, the homogeneous decomposition of water can be eliminated as a source. However, a likely source of permeating hydrogen is the reaction:

$$H_2O + Ni = NiO + H_2 \qquad (1)$$

For the temperature of 800°C., equilibrium in this reaction can be expressed by the equation:

$$(H_2)/(H_2O) = \text{keq.} = 3.1 \times 10^{-3} \qquad (2)$$

If it is assumed that hydrogen partial pressure was equal to the observed equilibrium pressure, Equation (2) yields water partial pressures of a reasonable order of magnitude. For example, the calculated value of water concentration in the delivery gas used for Runs A-5 and A-6 is less than 0.1% as compared to a measured value of 0.4%.

Limited water availability and/or buildup of a permeation barrier at the membrane surface have been dismissed as the primary cause of equilibrium pressure; however, one or both may have had a secondary effect. In several runs, it was observed that when permeation was resumed (after establishing equilibrium pressure) the new rates appeared lower than the original.

Another interesting observation was that the equilibrium pressure would slowly drop off with time. This was probably caused by permeation of hydrogen through the vacuum enclosure into the argon furnace atmosphere coupled with a reduced rate through the membrane.

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