

CF₂Cl₂ in one hour at temperatures up to 500° or between CH₃F and HF up to 400° in one hour. Higher temperatures could not be used because of chemical decomposition or reaction with the wall. No radioactivity was ever observed on the reactor wall, confirming the absence of exchange between HF and NiF₂ reported by Rogers and Katz.³ Our results emphasize the remarkable stability of the carbon-fluorine bond.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY⁴
OAK RIDGE, TENNESSEE

(3) M. T. Rogers and J. J. Katz, *THIS JOURNAL*, **74**, 1375 (1952).

(4) Operated by Carbide & Carbon Chemicals Corp. under Contract W-7405 for the U. S. Atomic Energy Commission.

Concentration Profiles in Packed-bed Ion-exchange Systems

BY E. B. BYRNE AND L. LAPIDUS

RECEIVED AUGUST 25, 1955

In recent years, considerable theoretical effort has been expended to describe the behavior of fixed bed percolation columns. Implicit in all of this work was the assumption of a flat velocity or concentration profile as the solute moves down the bed. Experimental verification or rejection of this assumption has not been considered in any detail. Baddour, *et al.*,¹ and Glueckauf and Coates² have briefly mentioned the problem in their ion-exchange studies, while Stewart³ has shown that adsorption on alumina oxide may produce considerable spreading of the concentration band at any column cross-section. Klinkenberg⁴ has also mentioned data collected indicating large variations in fluid velocity in a number of percolation processes.

In this note, the present writers would like to describe briefly a series of experiments in which concentration profiles between acidic and basic forms of an anion-exchange resin, Amberlite IRA-400, were observed.

The main piece of equipment was 10 inches long, 1 inch ID stainless steel column packed with exchange resin to a depth of 8 inches. A 1 inch layer of 1/2 mm. glass beads was placed on top of the resin to act as flow distributor, and glass wall plugs were placed at both ends to retain the beads and the resin. The column was constructed of two milled, semi-cylindrical sections, held together with two pressure clamps. By removing the clamps, the column could be split into two halves. Means were provided for feeding solution at a constant rate to the top of the column as well as for regeneration of the resin and backwashing of the bed proper. Various acids and bases were used both as regenerants and as solutes. These included acetic acid, sulfuric acid and sodium hydroxide. After the concentration profile had progressed to the desired point in the column, the solution was stopped, and 35 ml. of phenolphthalein solution added. The pressure clamps were removed; and the column, including the resin, was slit in a longitudinal direction. As a result, a cross-section of the entire column was available for observation with the acidic and basic portions being colored either a bright red or a neutral color.

The results indicate two distinct types of concentration profiles. The first, occurring when an acid solution percolated through the resin in the

basic form, was characterized by a flat profile. This profile maintained its shape throughout the length of the bed. The second, occurring when a basic solution flowed through the acid form resin, resembled sections of an inverted paraboloid or a frustrum of a paraboloid. In the second case, the concentrated wave at the wall was as much as 4 inches ahead of the center section. These two radically different profiles are intimately connected with the swelling and shrinking of the resin as the exchange process takes place. The uniform band occurs when the resin expands during reaction and the non-uniform band when shrinkage occurs. Expansion of the resin tends to flatten the concentration profiles since, as the flow in a localized area advances ahead of the main flow, expansion of the particles reduces the size of interstices between the particles and increases resistance to flow. Shrinkage, on the other hand, tends to accelerate the flow in areas where local flow has advanced ahead of the main flow. This was particularly true near the walls of the column where the resin mass tended to shrink away from the walls, thus producing channels where the flow could advance farther and farther ahead of the main flow. Because of this accelerated flow near the walls of the column, it is possible for basic solution to pass through the entire column almost unreacted, even though the full exchange capacity of the column has not been used.

Thus, the assumption of a flat concentration profile in an ion exchange column would seem to be valid only if the exchange reaction is such that swelling of the resin takes place.

SCHOOL OF ENGINEERING
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

Equilibrium Constants for the Formation of Complexes between 1,3-Diamino-2-propanol and Various Metal Ions¹

BY ELY GONICK, W. CONARD FERNELIUS AND BODIE E. DOUGLAS

RECEIVED SEPTEMBER 22, 1955

Compounds in which 1,3-diamino-2-propanol is present in the form of complexes with metal ions have been isolated.^{2,3} However, no data are available to permit comparison of the stability of these complexes with those containing no hydroxyl group. Such data are presented here.

Experimental

1,3-Diamino-2-propanol as obtained from Eastman Kodak Company was refluxed over barium oxide for four hours and distilled at 5 mm. The fraction boiling at 114° melted 40–42° and was found to possess the theoretical equivalent weight on titration.

Details of the experimental procedure are the same as those previously described.⁴

The terms used here and the method of calculation of con-

(1) Abstracted from a portion of a thesis presented by Ely Gonick in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951.

(2) F. G. Mann, *J. Chem. Soc.*, 2904 (1927).

(3) J. G. Breckenridge and J. W. R. Hodgins, *Can. J. Research*, **17**, 331 (1939).

(4) E. Gonick, W. C. Fernelius and B. E. Douglas, *THIS JOURNAL*, **76**, 4671 (1954).

(1) R. F. Baddour, D. J. Goldstein and P. Epstein, *Ind. Eng. Chem.*, **46**, 2192 (1954).

(2) E. Glueckauf and J. I. Coates, *J. Chem. Soc.*, 1315 (1947).

(3) A. Stewart, *Disc. Faraday Soc.*, **7**, 65 (1949).

(4) A. Klinkenberg, *ibid.*, **7**, 151 (1949).

TABLE I
FORMATION CONSTANTS OF $(\text{H}_2\text{NCH}_2)_2\text{CHOH}$ WITH VARIOUS METALS IN 1.0 M KNO_3 SOLUTION
Values for $(\text{H}_2\text{NCH}_2)_2\text{CH}_2$ and $(\text{H}_2\text{NCH}_2)_2\text{C}(\text{CH}_3)_2$ included for comparison.

	$(\text{H}_2\text{NCH}_2)_2\text{CHOH}$		$(\text{H}_2\text{NCH}_2)_2\text{CH}_2^6$		$(\text{H}_2\text{NCH}_2)_2\text{C}(\text{CH}_3)_2^6$	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
H^+ , 0°	10.65	9.14	11.60	9.95	11.22	9.07
30°	9.68	8.23	10.54	8.95	10.22	8.18
50°	9.11	7.69	9.92	8.38	9.65	7.55
Ag^{++} , 30°	5.80				4.66	
Co^{++} , 30°	3.90	3.24			4.88	3.07
Ni^{++} , 0°	6.19	4.88	7.00	4.92	7.22	4.99
30°	5.64	4.38			6.59	4.41
50°	5.37	4.01			6.23	4.15
Zn^{++} , 30°	4.60	4.42			5.21	5.20

stants are those given by Carlson, McReynolds and Verhoek.⁵ The calculated constants are given in Table I.

1,3-Diamino-2-propanol is a somewhat weaker base than either 1,3-diaminopropane or 2,2-dimethyl-1,3-propanediamine. The complete agreement in the N values for all three amines (except for Cu^{++}) indicates that the $-\text{OH}$ group is not active in coordination. The complexes of 1,3-diamino-2-propanol with Co^{++} , Ni^{++} and Zn^{++} are less stable than those of 2,2-dimethyl-1,3-diaminopropane with the same ions. Similarly, the Ni^{++} complexes are less stable than those of 1,3-diaminopropane. The system Cu^{++} -1,3-diamino-2-propanol is anomalous in that \bar{n} reaches a maximum value of 1.5.

(5) C. A. Carlson, J. P. McReynolds and F. H. Verhoek, *THIS JOURNAL*, **67**, 1334 (1945).

(6) G. B. Hares, W. C. Fernelius and B. E. Douglas, *ibid.*, accepted.

COLLEGE OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
STATE COLLEGE, PA.

The Preparation of *cis*- and of *trans*-Dichloro-bis-*l*-propylenediaminecobalt(III) Chloride^{1,2}

BY SR. MARY MARTINETTE, B.V.M., JOAN BUSCH AND
MILDA GULBINSKAS

RECEIVED JULY 6, 1955

The preparation of *cis*- and of *trans*-dichloro-bis-*l*-propylenediaminecobalt(III) chloride was first reported by Werner and Fröhlich.³ This method was later modified by Bailar and co-workers.⁴ We wish to report a semi-micro preparation which is a further modification of the original procedure. By making a careful study of the acidity requirements and of the procedure for oxidizing cobalt(II) to cobalt(III) the time required has been greatly diminished and the product is obtained without difficulty. The original method often yielded a product which could not readily be converted from *trans* to *cis*, possibly because of a residual acid condition; consequently the product was of questionable purity. The ready conversion from *trans* to *cis* has been considered a good index of purity. Use of 30% H_2O_2 cuts down the original 16 hours of aera-

(1) From the B.S. theses of Misses Joan Busch and Milda Gulbinkas.

(2) Aided by a grant from Research Corporation.

(3) A. Werner and A. Fröhlich, *Ber.*, **40**, 2225 (1907).

(4) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, *THIS JOURNAL*, **61**, 2402 (1939).

tion time to about 10 minutes. The original method gave yields from 35 to 45%. This method gives yields of from 45 to 55%.

Experimental

Preparation of the *trans* Form.—A flask containing 3.8 ml. of *l*-propylenediamine (resolved by the method of Baumann⁵ as modified by Bailar and co-workers⁴ and further modified by Jonassen⁶) and 4.76 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was immersed in an ice-bath. While swirling the solution in the reaction vessel 3 ml. of 30% H_2O_2 was added cautiously. On removal from the ice-bath, 25 ml. of concd. HCl (sp. gr. 1.18, 34% HCl) was added slowly. The resulting solution was concentrated to one-third of its original volume by passing a stream of air over it, keeping the temperature below 80°. The green crystals formed, *trans*- $[\text{Co-}l\text{-pn}_2\text{Cl}_2]\text{Cl}$, were separated from the solution by filtration, washed with ether and dried in an oven below 80°.

Conversion to the *cis* Form.—The dried crystals of the *trans* salt were dissolved in a minimum of water and the solution carefully neutralized with dilute (1:4) NH_4OH to a pH of approximately 7. On evaporation of this solution on a steam-cone, purple *cis*- $[\text{Co-}l\text{-pn}_2\text{Cl}_2]\text{Cl}$ formed as a glassy solid. The extreme solubility of the compound in water and the fact that it must be converted to the *cis* form in a neutral solution seems to make the preparation as a glassy solid imperative. Solubility studies made in this Laboratory have failed to yield any solvent from which it may be crystallized. This entire preparation was carried out in less than 4 hours.

(5) G. Baumann, *Ber.*, **28**, 1180 (1895).

(6) H. B. Jonassen, Thesis, University of Illinois, 1946.

DEPARTMENT OF CHEMISTRY
MUNDELEIN COLLEGE FOR WOMEN
CHICAGO, ILLINOIS

Basic Equilibrium Constants of Nitroguanidine and Nitroaminoguanidine

BY LILA M. HALL, JOHN E. DE VRIES AND E. ST. CLAIR
GANTZ

RECEIVED SEPTEMBER 26, 1955

The basic equilibrium constants of nitroguanidine and nitroaminoguanidine are extremely small. Consequently accurate determination of these values has not been possible by the usual titrimetric procedures. In connection with a study of the reactions of nitroguanidine in strongly acidic solutions,¹ it was observed that the small peak at 220–225 $m\mu$ increased with increasing acidity. The family of curves obtained showed a sharp isobestic point at 240 $m\mu$ between the minor (225 $m\mu$) and major (265 $m\mu$) absorption peaks, Fig. 1. The 265 $m\mu$ peak did not shift appreciably

(1) W. W. Brandt, J. E. De Vries and E. St. C. Gantz, *Anal. Chem.* **27**, 392 (1955).