# The Exchange of Water between Co+++ aq and the Solvent and between Co++ aq and the Solvent

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nance occurs between these levels, it seems possible there might be a weak line in the region of 1230 cm$^{-1}$. If 1236 cm$^{-1}$ is accepted as the $B_{1g}$ frequency, then the most likely one for $B_{2u}$ is still 995 cm$^{-1}$, leaving 810 cm$^{-1}$ as the Coriolis-perturbed twisting mode again.

[1] Rank, Shull, and Axford, J. Chem. Phys. **18**, 116 (1950).
[2] R. L. Arnett and B. L. Crawford, Jr., J. Chem. Phys. **18**, 118 (1950).
* The existence of weak temporary induced dipoles has recently been suggested [D. H. Whiffen, Trans. Faraday Soc. **46**, 124 (1950)] as the explanation of the observed dielectric losses in the liquid microwave spectra of molecules having no permanent moment. Such temporary molecular asymmetry, for which there was previously no very definite evidence, would be the cause of any breakdown of selection rules in the liquid state.
The liquid-vapor shift in methyl mercaptan for $\nu SH$ has recently been reported [H. W. Thompson and C. H. Miller, Trans. Faraday Soc. **46**, 22 (1950); cf. H. W. Thompson and N. P. Skerrett, Trans. Faraday Soc. **38**, 812 (1940)] as 2607 to 2572 cm$^{-1}$; there may well be weak hydrogen-bonding here.
[3] P. Torkington, Proc. Phys. Soc. (to be published).

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# Comment on "Thermodynamic Properties of the Surface of Magnesium Oxide"

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March 10, 1950

RECENTLY Jura[1] has pointed out the possibility of the experimental determination of the thermodynamic properties of solid surfaces. While the method indicated is undoubtedly correct, the results depicted in Fig. 1 of the paper are thermodynamically inconsistent.

The relationship between $\gamma$ and $h$ is the well-known one

$$h = \gamma - T(\partial \gamma / \partial T)_\Sigma$$

from which it follows that if $(\partial \gamma / \partial T)_\Sigma$ is positive then $\gamma$ must at all temperatures be greater than $h$, not less than $h$ as indicated in Jura's Fig. 1.

However, there is evidence to suggest that $(\partial \gamma / \partial T)_\Sigma$ may indeed be negative for the particular solid system considered. Thermodynamics requires that

$$(\partial \gamma / \partial T)_\Sigma = -(\partial S / \partial \Sigma)_T,$$

where $S$ is the total entropy of a body with a surface. The data concerning the difference in thermal properties of fine and coarse particles of magnesium oxide, considered by Giauque[2] require that $(\partial S / \partial \Sigma)_T$ be positive, from which it follows that $(\partial \gamma / \partial T)_\Sigma$ must be negative. It is, therefore, suggested that the positive value of $(\partial \gamma / \partial T)_\Sigma$ in Jura's Fig. 1 is incorrect.

Further, it should be noted that theoretical treatments exist which also lead to this conclusion. Several years ago Brager and Schuchowitzky[3] derived an explicit expression for the heat capacity of a solid taking into account the influence of the surface. They attempted to use this to evaluate the extent of surface of a solid. Huang and Wyllie[4] have evaluated the free surface energy of some metals, and have used in part the Brager and Schuchowitzky development.

[1] G. Jura, J. Chem. Phys. **17**, 1335 (1949).
[2] W. F. Giauque, J. Am. Chem. Soc. **71**, 3192 (1949).
[3] A. Brager and A. Schuchowitzky, Acta Physicochimica (URSS) **21**, 1001 (1946). A development along similar lines has been given by Montroll, J. Chem. Phys. **18**, 183 (1950).
[4] K. Huang and G. Wyllie, Proc. Phys. Soc. **A62**, 180 (1949).

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# The Hydrogen Exchange of Alkali Amides and Hydroxide with Deuterium Gas

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March 13, 1950

RECENTLY[1] two of us reported the catalytic conversion of parahydrogen by liquid ammonia solutions of the alkali metals; the detailed kinetics of this process will be reported in the near future. Since alkali metal solutions may contain amide ion impurity, it was necessary to show that the observed conversion was not due to amide impurities. This became especially important when it was discovered that ammonia solutions of potassium amide, even at $-50°C$, effect the conversion at rates comparable to those of the metal solutions. However, the amide solutions not only effect the ortho-parahydrogen conversion but also exchange with deuterium gas while the metal solutions show no such exchange, indicating the absence of amide. It would appear that the amide conversion, unlike the alkali metal process, proceeds through a chemical mechanism. In view of unpublished data, this difference is to be expected since the alkali-metal conversion appears to occur through a paramagnetic catalysis.

That amide should exchange at all with deuterium at these temperatures is somewhat unexpected in view of the fact that the thermal exchange with ammonia[2] cannot be conveniently studied much below 500°C and the exchange with hydroxide is difficult to measure below 90°.[3,4] Consequently, the exchange seemed of sufficient importance to justify a brief report although the experiments are being continued to include a general study of the exchange of deuterium gas with strong bases.

The rapidity with which this exchange proceeds is indicated by data from a typical experiment. A 0.001$M$ solution of potassium amide has a half-life of less than one minute for the exchange in solution. The molar rate constant appears to increase with dilution, suggesting that the amide ion is the catalytic species. Most of the early measurements were studied using parahydrogen rather than deuterium because it simplified the analysis of the gas mixtures by the Pirani gauge technique.[5] We are still uncertain as to whether the hydrogen deuteride appears as an intermediate, but analyses using the mass spectrograph are under way to clarify this point.

The homogeneous nature of the hydroxide catalyzed exchange between deuterium oxide and hydrogen was first reported by Bonhoeffer.[3] Abe[4] later stated that the hydroxide solutions, if dialized or heated at 100°C for some time, lost their catalytic activity.

Our studies on the system deuterium, water and potassium hydroxide indicate that the reaction is not affected by either light or increase in glass surface, and, contrary to Abe's observations, that the catalytic activity cannot be destroyed. Abe attributed the activity to iron impurities, but this is unlikely since in our experiments, C.P. sodium hydroxide and potassium hydroxide, either C.P. or prepared from distilled metallic potassium, do not differ in activity.

The reaction is, within the limit of our experimental error, first order with respect to both deuterium gas and hydroxide ion. The process has a high temperature coefficient and the reported lack of reproducibility appears to arise from inadequate temperature control.

[1] Y. Claeys, C. Baes and W. Wilmarth, J. Chem. Phys. **16**, 425–6 (1948).
[2] A. Farkas, Trans. Faraday Soc. **32**, 416–27 (1936).
[3] K. Wirtz and K. F. Bonhoeffer, J. Physik. Chem. **177A**, 1–6 (1936).
[4] S. Abe, Sci. Papers, Inst. Phys. Chem. Research (Tokyo) **38**, 287–97 (1941).
[5] J. L. Bolland and H. W. Melville, Trans. Faraday Soc. **33**, 1316 (1937).

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# The Exchange of Water between Co$^{+++}_{aq}$ and the Solvent and between Co$^{++}_{aq}$ and the Solvent*

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March 10, 1950

IN a continuation of the experiments on the exchange of water between hydrated cations and the solvent, a study of the exchange with Co$^{+++}$ was undertaken. This ion was chosen for early study since the rates of replacement of one ligand by another are slow in almost all of its complex ion reactions. It seemed probable, therefore, that the exchange of water coordinated to cobaltic ion with the solvent water would be slow enough to

permit the determination of the coordination number of the ion for water.

The exchange experiments with cobaltic ion are made difficult because this ion, particularly at high concentrations, oxidizes water fairly rapidly. Solutions of cobaltic perchlorate in perchloric acid were obtained by electrolytic oxidation of cobaltous perchlorate, and always contained cobaltous ion at concentrations about equal to that of cobaltic ion. The exchange experiments were conducted as described for $Cr^{+++}$ with the difference that the various samples of water were obtained by successive distillations from a single sample of the solution in each experiment. Before the last water sample was taken, a portion of the solution was removed for analysis for $Co^{+++}$ and then excess anhydrous hydrazine sulfate was added to the remainder of the solution to reduce the cobaltic ion to cobaltous ion. Separate experiments have shown that water is exchanged very rapidly between $Co^{++}_{aq}$ and solvent; hence the isotopic composition of water in the final reduced sample corresponds to complete exchange. The data obtained in three experiments on the cobaltic ion exchange are presented in Table I.

TABLE I. Exchange of water between aqueous cobaltic ion and the solvent.

(Part A describes the composition and handling of the solution; Part B, the results of the isotopic analysis on the samples of water removed at the indicated intervals. Concentration is expressed as molality, time in minutes. $N$ is the ratio $O^{18}/(O^{16}\pm O^{18})$ in water. Temperature, $O\pm 4°$.)

Part A

| Experiment No. | | 1 | 2 | 3 |
|---|---|---|---|---|
| $(Co^{+++})$ | | 0.510 | 0.430 | 0.406 |
| (Total Co) | | 1.203 | 0.968 | 0.914 |
| $(H^+)$ | | 4.22 | 4.67 | 4.10 |
| $(ClO_4^-)$ | | 7.14 | 6.61 | 6.34 |
| Expected decrease in $10^3N$ for slow exchange[a] | | 0.24 | 0.26 | 0.20 |
| Time elapsed between mixing and final analysis | | — | 19.0 | 47.5 |
| % decomposition of $Co^{+++}$ in this interval | | — | 1.9 | 4.4 |
| Fraction of total water removed by distillation | | 0.52 | 0.20 | 0.14 |

Part B

| Experiment No. 1 | Time | 2.3 | 11.7 | 21.2 | 27.0 | ∞ |
|---|---|---|---|---|---|---|
| | $10^3N$ | 5.818 | 5.827 | 5.856 | 5.879 | 5.828 |
| Experiment No. 2 | Time | 2.7 | 9.2 | 15.2 | ∞ | ∞ |
| | $10^3N$ | 6.313 | 6.327 | 6.330 | 6.356 | 6.370 |
| Experiment No. 3 | Time | 2.2 | 14.4 | 30.1 | 43.3 | ∞ |
| | $10^3N$ | 6.114 | 6.103 | 6.114 | 6.084 | 6.138 |

[a] This represents the total change in $10^3N$ expected if each $Co^{+++}$ held back six molecules of water initially and then exchanged them during the course of the experiment.

The results show that the change in $N$, the isotopic composition, during each experiment is much smaller than that predicted on the basis of slow exchange of six water molecules per cobaltic ion. Indeed, the trend in $N$ is in the opposite direction from that expected for slow exchange, and this trend has about the magnitude expected for that which would result from the fractionation of the water on repeated distillation (cf. the experiments with $Co^{++}_{aq}$). It may be concluded therefore that the exchange of water between aqueous cobaltic ion and the solvent is essentially complete under the conditions of our experiments by the time of the first sampling.

This result is surprising in view of the slow rates of substitution observed for Co(III) in all of the complex ions described for it. It is possible that the exchange of $H_2O$ in this system does not proceed by direct substitution on $Co^{+++}$, but chooses an alternative path. If the electron exchange between aqueous cobaltous ion and cobaltic ion is rapid,[1] then $Co^{++}_{aq}$ will be an efficient catalyst for the $Co^{+++}_{aq}$–$H_2O$ exchange, since $Co^{++}_{aq}$ does exchange coordinated water rapidly with the solvent. Further experiments are being made to measure the $Co^{+++}_{aq}$–$H_2O$ exchange at much lower concentrations of $Co^{++}_{aq}$.

The observations on the exchange of $H_2O$ between $Co^{++}_{aq}$ and the solvent are presented in Table II.

TABLE II. Exchange of $H_2O$ between $Co_{aq}^{++}$ and solvent.

| Experiment 1 | | | |
|---|---|---|---|
| $(Co^{++})=1.545$ molal; $(H^+)=3.00$ molal. Temperature $1°\pm 1°$. | | | |
| Time, min. | 2.0 | 12.2 | 1600[a] |
| $10^3N$ | 6.490 | 6.505 | 6.512 |

| Experiment 2 | | |
|---|---|---|
| $(Co^{++})=1.68$ molal; $(H^+)=1.68$ molal. Temperature $1°\pm 1°$. | | |
| Time, min. | 2.5 | 34 |
| $10^3N$ | 5.593 | 5.589 |

[a] The solution was allowed to warm up to room temperature in the interval between the end of the second distillation and the beginning of the third.

The data necessary for computing precise isotope balances in Experiment 2 were obtained. The value of $N_\infty$ calculated for random mixing in the liquid is $5.660\times 10^{-3}$, which agrees with the observed values of $N$ within about the fractionation factor for distillation. The value of $N_0$ calculated for initial holdback of $6H_2O$ for each $Co^{++}$ is $6.469\times 10^{-3}$. For Experiment 1, $N_\infty$ calc. and $N_0^6$ are ca. $6.52\times 10^{-3}$ and $7.43\times 10^{-3}$ respectively. The experiments prove that the exchange is complete within the time of the first sampling.

The isotope analyses were made in the laboratory of Professor Harold C. Urey of the Institute for Nuclear Studies, The University of Chicago, with the generous assistance of Dr. Samuel Epstein.

[1] Hoshowsky, Holmes, and McCallum, Can. J. Research 27, No. 4, 258 (1949), using various separation procedures, have observed complete electron exchange in this system within the time of separation of the ions.

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### Erratum: Photolysis of Methyl Iodide
[J. Chem. Phys. 18, 194 (1950)]

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THE sentence on page 195 pertaining to the infra-red analytical method should read: "$CH_4$ absorption at $7.7\mu$, $C_2H_6$ at $6.8\mu$, $C_2H_4$ at $10.6\mu$ and $C_2H_2^4$ at $13.7\mu$ were used for the analysis."

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### Ground State Splittings in the Iron Group, Particularly Cobaltous Ion. The Operation of Kramer's Rule

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March 21, 1950

THE theoretical treatments of the susceptibility of paramagnetic salts, such as that of Schlapp and Penney[1] who have been quite successful with the rare earths and with many of the iron group salts, have met with little success in the interpretation of the data on those of cobalt. Bose,[2] in comparing his recent measurements on the principle susceptibilities of two double salts of cobaltous sulfate down to 80°K with the theory of Schlapp and Penney,[1] was able to choose between the two possibilities they suggested but was unable to get an over-all agreement between theory and experiment. Schlapp and Penney[1] had discarded as incorrect the hydrogen temperature data of Jackson,[3] which could not be made to fit the theory. Bose corrected Jackson's data for numerical errors, but was still unable to fit the theory to all of the low temperature data.