

after cooling, to titrate for iron with titanium. Check determinations with "cupferron" agreed fairly well (Table XI). No doubt the same procedure would serve for the rapid determination of iron in manganese ores.

TABLE XI.

| Analysis. | Sample No. | Fe ₂ O ₃ found. Ti ₂ (SO ₄) ₃ . % | Fe ₂ O ₃ found. C ₈ H ₅ .NO.NONH ₄ . % |
|-----------|------------|---|---|
| 1..... | 13 | 20.44 | 20.51 |

XVI. Conclusions.

The method of Knecht and Hibbert for the estimation of iron is both rapid and accurate and it may be used with advantage under a great variety of circumstances.

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THE LOWERING OF THE VAPOR PRESSURE OF WATER AT 20° PRODUCED BY DISSOLVED POTASSIUM CHLORIDE.¹

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Introduction.

The work described in this article is a continuation of the measurement of the vapor pressure of solutions by an improved static method devised by Frazer and Lovelace, which has been described in detail in former articles.² The chief difficulty encountered in making vapor pressure measurements by this method has been the complete removal of air from the solutions. In the former work it was attempted to rid the solutions of the final traces of air after they had been introduced into the system by an oft-repeated series of operations consisting in expanding the vapor phase into large bulbs, then trapping off the solution and evacuating the bulbs. The residual air pressure was determined by absorbing the water vapor in the bulbs with phosphorus pentoxide and reading the air pressure with a McLeod gage. At that time a period of overnight was thought to be necessary for the absorption of the water vapor, but at the beginning of the work described herein it was established that in this time an appreciable amount of air will be adsorbed on the pentoxide and upon the walls of the system, thus giving an erroneous idea of the amount of air present. It seemed quite certain that some of the former measurements had been inaccurate owing to traces of air, so more rigorous measures

¹ The experimental part of this paper is taken from the dissertation submitted by V. B. Sease to the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Frazer and Lovelace, *THIS JOURNAL*, 36, 2439 (1914); Lovelace, Frazer and Miller, *ibid.*, 38, 515 (1916).

were employed for ridding the solutions of air. A method, described in a former article,¹ was devised for removing the air from the solutions prior to their introduction into the system. In making tests for residual air in these solutions the reading on the McLeod gage would be negligible in 15 to 20 minutes. It therefore, seemed advisable with solutions thus prepared air-free to repeat the measurements of potassium chloride solutions, extending the work to more dilute and to more concentrated solutions than had formerly been measured.

Apparatus.

The apparatus used in this work was essentially the same as that described in a former article.² No changes were made in the bath design nor in the thermoregulation. An extra trap was placed in the system³ connecting a point to the right of Trap 11 with a point to the right of Trap 5, thus making it possible to balance the vapor pressure of one solution against that of another in the Rayleigh manometer. As the range of the manometer was limited it was necessary to devise this means for reading the lowering of the more concentrated solutions. For example, a 1.5 *M* solution was read against the solvent, then a 3.0 *M* solution against the 1.5 *M*; the 3.0 *M* solution was left in the bath and solutions of higher concentration read against it.

A silver millimeter scale and a more powerful telescope were installed for reading the deflections of the manometer. The difficulties in illuminating a metallic scale had forced the use of a paper scale hitherto, but a frosted glass plate set in an ordinary photographer's dark-room lantern fitted with a tungsten lamp was found to give excellent illumination of the metallic scale.

Experimental Procedure.

The potassium chloride used in this investigation was the best obtainable material with guaranteed analysis, and was recrystallized from freshly distilled water, using centrifugal drainage. Careful tests for impurities were negative. Quantitative determinations of chlorine by 2 methods gave results that were 0.1 or 0.2% below theoretical. This indicated an impurity which was afterwards found to be water. The samples for analysis had been dried at 150° overnight. It was not necessary to dry potassium chloride intended for making up solutions, as the solutions were prepared at approximate concentration and analyzed by means of the interferometer for exact concentration after the measurements were completed. But for the interferometer standards it was necessary to dry the potassium chloride to constant weight at 300° in order to remove the last traces of water.

¹ Frazer, Lovelace and Rogers, *THIS JOURNAL*, 42, 1793 (1920).

² Lovelace, Frazer and Miller, *loc. cit.*

³ *THIS JOURNAL*, 38, 521 (1916), Fig. 3.

Before introducing the solution, the entire system was evacuated by intermittent pumpings for a period of 24 to 36 hours. The method of making up and introducing the solution into the system was essentially the same as the modified procedure described in a former article¹ on the lowering of vapor pressure of water by dissolved mannite. It is to be noted that according to this procedure the concentration of the solution is known only approximately at the time observations of pressure are being made, the exact concentration being determined by means of the interferometer after the solution is removed from the apparatus.

With careful manipulation, the solutions thus introduced showed negligible amounts of air in tests made after 4 to 6 twelve-hour expansions of the vapor phase. The more concentrated solutions did not become air-free quite so rapidly, owing perhaps to the difficulty of pumping off the air adsorbed on the solid salt prior to mixing with the solvent. After the tests showed that the solutions contained a negligible amount of air, readings were taken on the manometer alternately by different observers until about 6 sets of reading extending over a period of 2 to 4 days were obtained. The procedure was to take a zero point with both limbs of the manometer connected with the same system, generally that one containing the solvent and its vapor. Then immediately the traps were adjusted so that the vapor of the solvent was in one limb of the manometer and the vapor of the solution was in the other. After allowing 10 or 15 minutes for the establishment of equilibrium, the manometer was set and a reading taken. The manometer was then shifted and reset, until at least 3 readings were taken, and averaged. The difference between this average and the mean zero point gave the deflection of the solution. Owing to the unfortunate situation of the laboratory near heavy street and railway traffic the zero point sometimes shifted during the readings. No reading, therefore, was regarded as reliable unless the zero point was afterwards checked within the limits of accuracy in setting the manometer. Under quiet conditions, the manometer was easily set to 0.1 mm. scale deflection. As one mm. on the scale corresponds to 0.00511 mm. actual difference in level of the meniscuses in the manometer, this gave a precision in setting of approximately 0.0005 mm.

The statement in former articles that exact regulation of the temperature of the vapor phase of the system is unnecessary was rigorously tested out and confirmed. It is absolutely essential that the temperature of the solution be very closely regulated, but around the vapor phase of the system it is only necessary to avoid air currents and sudden changes in temperature.

Calculations and Method of Analysis.

The method of calculating the lowering of vapor pressure has been

¹ Frazer, Lovelace and Rogers, *loc. cit.*

fully described in former articles, as also the use of the Zeiss interferometer as a means of determining the concentrations of the solutions after observations of pressure have been completed. Every precaution was taken to reduce to a minimum the errors involved in the use of the interferometer.

Owing to the fact that solvent was allowed to remain in the apparatus for several months at a time, there was a possibility of a slight action on the glass. In order to see whether any measurable error resulted from such action, the solvent, on coming from the bath, was always tested in the interferometer against freshly distilled water. On one occasion fresh solvent was introduced in one of the solution bulbs and its vapor pressure balanced against that of the old solvent. In no case were the findings sufficient to change any of the results.

Experimental Data.

The vapor pressure lowerings for solutions ranging from 0.05 M to 4.0 M are recorded in Table I. In all cases the recorded value is the mean of from 5 to 7 sets of observations made over a period of from 2 to 3, days, after complete removal of dissolved air. In all measurements, the maximum deviation of the mean of each set of observations from the final mean of all is less than 0.001 mm.

TABLE I.

M = concentration in gram moles of KCl per 1000 g. of solvent.
 $P_0 - P_1$ = observed lowering in mm. of mercury, corrected to mercury at 0°.
 $\frac{P_0 - P_1}{M}$ = molecular lowering.

| $T = 20^\circ.$ | | |
|-----------------|--------------|----------------|
| $M.$ | $P_0 - P_1.$ | $P_0 - P_1/M.$ |
| 0.0498 | 0.0293 | 0.5888 |
| 0.0704 | 0.0408 | 0.5799 |
| 0.0997 | 0.0573 | 0.5744 |
| 0.2013 | 0.1136 | 0.5641 |
| 0.2985 | 0.1672 | 0.5600 |
| 0.3855 | 0.2144 | 0.5562 |
| 0.4973 | 0.2770 | 0.5569 |
| 0.6000 | 0.3347 | 0.5579 |
| 0.6995 | 0.3899 | 0.5573 |
| 0.7958 | 0.4412 | 0.5544 |
| 0.9968 | 0.5525 | 0.5543 |
| 1.2461 | 0.6904 | 0.5540 |
| 1.5099 | 0.8383 | 0.5552 |
| 1.7072 | 0.9482 | 0.5554 |
| 1.9938 | 1.1077 | 0.5556 |
| 2.2450 | 1.2492 | 0.5564 |
| 2.4916 | 1.3893 | 0.5576 |
| 3.0017 | 1.6844 | 0.5611 |
| 3.5783 | 2.0203 | 0.5647 |
| 4.0070 | 2.2741 | 0.5675 |

Molecular Lowering.—The variation in lowering of vapor pressure with concentration is best seen when molecular lowering is plotted against concentration as in Fig. 1.

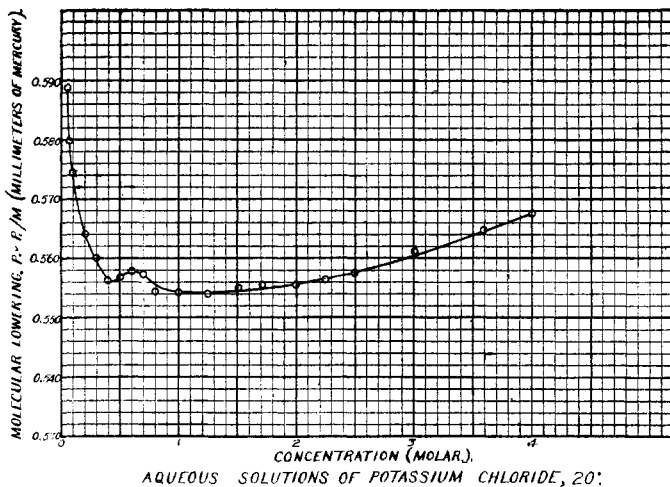


Fig. 1.

The 2 most striking features of this curve are the irregular shape in the region between 0.4 *M* and 0.8 *M*, and the fact that the curve finally passes through a distinct minimum at about 1.0 *M* concentration. The points of the curve between 0.4 *M* and 0.8 *M* were determined with great care and the irregularities here observed are entirely too great to be attributed to experimental error. We have no explanation to offer for the peculiar shape of the curve in this region other than possible changes in the state of molecular aggregation of the solvent. That the curve should finally pass through a minimum is probably due to changes in the degree of hydration of the solute.

Potassium chloride belongs to that class of salts whose solutions exhibit "negative viscosity," the concentration-viscosity curves passing through minima, where the viscosity is less than that of the solvent. While viscosity data on potassium chloride solutions at 20° are not available, reference to the values of Ranken and Taylor,¹ Gruneisen,² and Getman³ at adjacent temperatures, shows that the viscosity curve follows the molecular lowering curve in a very striking manner.

Calculation of Vapor-Pressure Lowering from Freezing-Point Data.

The equation connecting the mol fraction of the solvent, $N/N + n$, with the lowering of freezing point, Δt_F , is

¹ Ranken and Taylor, *Proc. Roy. Soc. Edinburgh*, **45**, 397.

² Gruneisen, *Wiss. Abh. Phys. Tech. Reichsunstalt*, **4**, 239.

³ Getman, *THIS JOURNAL*, **30**, 721 (1908); *J. chim. phys.*, **5**, 344 (1907).

$$\log \frac{N}{N+n} = \frac{\Delta C_P}{R} \log \frac{T_F}{T_{F_0}} - \frac{0.4343(L_{F_0} - \Delta C_P \Delta t_F)}{RT_F} + \frac{0.4343 L_{F_0}}{RT_{F_0}} \quad (1)$$

where ΔC_P is the difference in the molal heat capacities of the solvent in the liquid and solid states, L_{F_0} is the molal heat of fusion of the pure solvent at its freezing point, T_{F_0} the absolute freezing point of the solvent, T_F the absolute freezing point of the solution, and R is the ordinary gas constant.¹ From Raoult's law we get

$$\log \frac{N}{N+n} = \log \frac{P_1}{P_0} \quad (2)$$

Combining (1) and (2),

$$\log \frac{P_1}{P_0} = \frac{\Delta C_P}{R} \log \frac{T_F}{T_{F_0}} - \frac{0.4343(L_{F_0} - \Delta C_P \Delta t_F)}{RT_F} + 0.4343 \frac{L_{F_0}}{RT_{F_0}} \quad (3)$$

This equation is applicable for calculating the vapor pressure of a solution at its freezing point. If von Babo's law, which states that the relation between the vapor pressure of a solution and solvent is independent of temperature, holds, it is possible to use this equation for calculating the vapor pressure of a solution at 20° by substituting for P_0 the vapor pressure of pure solvent at 20°.

Calculations of vapor-pressure lowerings from freezing-point data for several concentrations of potassium chloride have been attempted, using the data of Roloff² and of Noyes and Falk.³ Noyes and Falk give the weighted mean of all recent reliable freezing-point observations up to 0.5 molar concentration. The data of Roloff were chosen as the best available for the more concentrated solutions; though they were not included in the weighted means of Noyes and Falk, they show good agreement where the concentrations overlap.

In making the calculations the value of ΔC_P was taken as 9.04. This figure was derived from a consideration of the heat capacity of water between 0° and -5° as given in Landolt-Börnstein, and of ice over the same temperature range as given in *Bureau of Standards Sci. Paper 248*. The values used for R and L_{F_0} were 1.985 and 1435.5 respectively. The value of P_0 at 20° is 17.539 mm. of mercury according to Scheel and Heuse.

The vapor-pressure lowerings calculated from freezing-point data are compared in Table II with the observed lowerings. Also in this table the values of $\log P_1/P_0$ calculated at the freezing point from freezing-point lowerings are given along with values calculated at 20° from vapor-pressure data gathered in this investigation. For von Babo's law to hold the change in $\log P_1/P_0$ with temperature should be zero, that is, the values at the freezing point and at 20° should be identical. Refer-

¹ Washburn, "Principles of Physical Chemistry," 1915, p. 169.

² Roloff, THIS JOURNAL, 32, 1020 (1910).

³ Noyes and Falk, Z. physik. Chem., 18, 578 (1895).

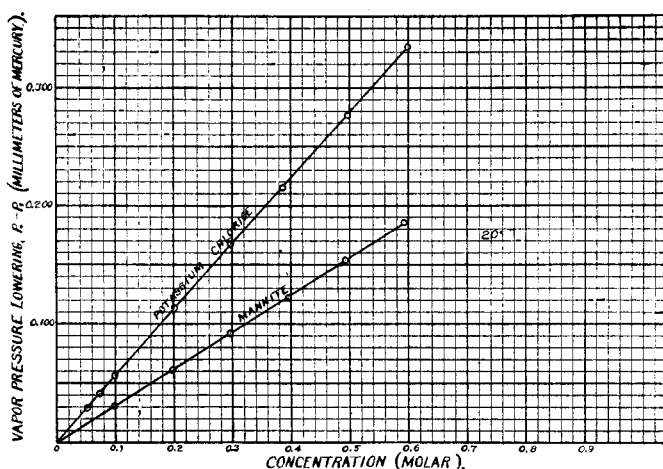


Fig. 2.

ence to the table shows rather close agreement of these values up to around 1.0 M concentration. The values calculated from vapor-pressure observations are from 1 to 3% lower than those calculated from freezing-point lowerings, but above 1.0 M they become increasingly larger, corresponding to the increased lowering observed in concentrated solutions shown by the rise in the molecular-lowering curve.

TABLE II.

Vapor-Pressure Lowerings of Potassium Chloride Solutions at 20° Calculated from Freezing-Point Data and Compared with Lowerings Observed in the Present Investigation.

| Conc. | Δt_F | $\text{Log } P_1/P_0$ | | $P_0 - P_1$ | | Difference. Calc. — Obs. |
|--------|--------------|-----------------------|----------|-------------|-----------|-----------------------------|
| | | At F. P. | At 20°. | Calculated. | Observed. | |
| 0.05 | 0.175 | -0.00074 | -0.00072 | 0.030 | 0.029 | 0.001 |
| 0.1 | 0.345 | -0.00145 | -0.00142 | 0.059 | 0.057 | 0.002 |
| 0.1121 | 0.384 | -0.00162 | -0.00159 | 0.065 | 0.064 | 0.001 |
| 0.2 | 0.679 | -0.00286 | -0.00281 | 0.115 | 0.113 | 0.002 |
| 0.2428 | 0.827 | -0.00348 | -0.00338 | 0.140 | 0.136 | 0.004 |
| 0.3 | 1.007 | -0.00425 | -0.00418 | 0.171 | 0.168 | 0.003 |
| 0.4 | 1.333 | -0.00562 | -0.00553 | 0.226 | 0.222 | 0.004 |
| 0.4136 | 1.389 | -0.00586 | -0.00578 | 0.235 | 0.232 | 0.003 |
| 0.5 | 1.665 | -0.00702 | -0.00694 | 0.281 | 0.278 | 0.003 |
| 0.8225 | 2.721 | -0.01149 | -0.01144 | 0.458 | 0.456 | 0.002 |
| 1.0473 | 3.437 | -0.01451 | -0.01463 | 0.578 | 0.581 | -0.003 |
| 1.4404 | 4.696 | -0.01984 | -0.02025 | 0.783 | 0.799 | -0.016 |
| 1.9488 | 6.37 | -0.02691 | -0.02768 | 1.054 | 1.083 | -0.029 |
| 2.2572 | 7.34 | -0.03105 | -0.03228 | 1.210 | 1.256 | -0.046 |
| 2.6730 | 8.66 | -0.03665 | -0.03867 | 1.420 | 1.494 | -0.074 |
| 3.3020 | 10.75 | -0.04554 | -0.04863 | 1.747 | 1.858 | -0.111 |

Calculation of Percentage Ionization.

The vapor-pressure lowerings for solutions of mannite investigated by this method¹ have been found to follow Raoult's law very closely. By comparing these measurements with the measurements of potassium-chloride solutions according to the following formula the percentage ionization of dilute solutions of potassium chloride was calculated:

$$\frac{(P_o - P_1)_{\text{KCl}}}{(P_o - P_1)_{\text{Mannite}}} - 1 = i$$

The curves shown in Fig. 2 were plotted on large coördinates and from them were interpolated the values for calculating the percentage ionization. The values calculated were compared in Table II with values obtained from the freezing-point and conductivity data compiled by Noyes and Falk.² The values under FP and CR are for concentrations expressed in mols per liter of solution, those under VP for concentrations in mols per 1000 g. of solvent. But it is probable that no more serious error is involved on account of the different modes of expressing concentration than might arise in the interpolation of the lowerings to even concentrations. The values given in Table III are plotted in Fig. 3. It will be

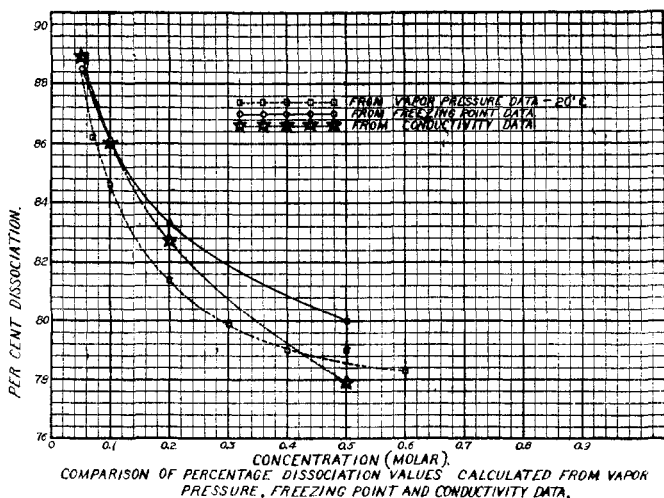


Fig. 3.

noticed that the curves calculated from freezing-point and vapor-pressure data are very similar to each other, and dissimilar to the curve calculated from conductivity data. This is to be expected, for in vapor-pressure

¹ Frazer, Lovelace and Rogers, *THIS JOURNAL*, 42, 1793 (1920).

² Noyes and Falk, *ibid.*, 34, 485 (1912).

and freezing-point observations the properties of the solvent are measured, while in conductivity observations the properties of the solute are measured.

The lack of closer agreement of the values under FP and VP cannot be attributed to the temperature coefficient of ionization. Noyes and Falk in discussing ionization values calculated from freezing-point and conductivity data at 18° state that the effect of temperature on ionization over such a short range of temperature as dealt with here is negligible. However, the temperature coefficient of hydration may be sufficient to account for the discrepancies observed.

TABLE III.

Percentage Ionization of Dilute Solutions of Potassium Chloride Calculated from Vapor-Pressure Lowerings and Compared with Values Calculated from Freezing-Point and Conductivity Data.

| Concentration. | $P_0 - P_1$ for KCl. | $P_0 - P_1$ for Mannite. | Percentage Ionization. | | |
|----------------|-------------------------|-----------------------------|------------------------|-----------|------|
| | | | VP (20°). | CR (18°). | FP. |
| 0.05 | 0.0294 | 0.0156 | 88.5 | 88.9 | 88.5 |
| 0.07 | 0.0406 | 0.0218 | 86.2 | .. | .. |
| 0.1 | 0.0574 | 0.0311 | 84.6 | 86.0 | 86.1 |
| 0.2 | 0.1128 | 0.0622 | 81.4 | 82.7 | 83.3 |
| 0.3 | 0.1680 | 0.0934 | 79.9 | .. | .. |
| 0.4 | 0.2225 | 0.1243 | 79.0 | .. | .. |
| 0.5 | 0.2785 | 0.1555 | 79.0 | 77.9 | 80.0 |
| 0.6 | 0.3347 | 0.1877 | 78.3 | .. | .. |

Summary.

The lowering of the vapor pressure of aqueous solutions of potassium chloride ranging from 0.05 *M* to 4.0 *M* has been measured by the improved static method of Frazer and Lovelace. A more rapid and efficient method for making up air-free solutions has been devised, and the measurements are believed to be accurate to 0.001 mm.

The molecular-lowering curve was found to be irregular at 20°, passing through a distinct minimum at about 1.0 *M* concentration.

The vapor pressures of potassium chloride solutions at 20° were calculated from freezing-point data by means of von Babo's law and an equation connecting freezing-point lowering with vapor pressure. The calculated values varied from about 3% greater than observed values in the dilute solutions to about 6% less than observed values in the concentrated solutions.

The percentage ionization of dilute solutions of potassium chloride was calculated by comparing the vapor-pressure lowerings with the lowerings produced by mannite and the value obtained agreed well with the best values from freezing-point and conductivity data.