

if the groups were free to move radially; and hence the orbital moment might not be quenched so much as it is in simpler compounds. A large amount of orbital contribution to the moment is also observed in the case of ferrihemoglobin cyanide and hydrosulfide,⁹ which, however, have only one unpaired electron per iron atom.

Summary

The magnetic moments of the iron atoms in

ferromyoglobin and ferrimyoglobin have been determined to be 5.46 and 5.85 Bohr magnetons, respectively. The magnetic moments indicate that the iron atoms are held by essentially ionic bonds in ferromyoglobin and ferrimyoglobin. The agreement of the magnetic moments with those calculated for the analogous hemoglobin compounds leads to the conclusion that magnetic interactions do not occur between the four hemes of hemoglobin.

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Activity Coefficients of Barium and Strontium Carbonates in Aqueous Solutions of Alkali Chlorides

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Townley, Whitney and Felsing¹ have computed activity coefficients of strontium and barium carbonates in alkali chloride solutions from solubility measurements in carbon dioxide-free, aqueous solutions at 25 and at 40°. We have been unable to check the calculations recorded in their tables and, while details of their computations are not given, it appears that they incorrectly computed the mean ion molality and have misinterpreted (K_2)'s taken from tables of MacInnes and Belcher² as stoichiometric second dissociation constants of carbonic acid in salt solutions whereas these K 's are in reality the products of the stoichiometric constants by the square of the mean activity coefficients of hydrochloric acid in the same solutions.³ Correction for the activity coefficients of hydrochloric acid is important in the higher concentrations of the salt solutions employed by Felsing and co-workers.

We have accordingly recalculated the activity coefficients and obtained results that differ from

(1) Townley, Whitney and Felsing, *THIS JOURNAL*, **59**, 631 (1937).

(2) (a) MacInnes and Belcher, *ibid.*, **55**, 2630 (1933); (b) **57**, 1683 (1935).

(3) The above misinterpretation is easily made for MacInnes and Belcher refer to their (K_2)'s as "apparent second ionization constants" and use them, without correction, as the stoichiometric constants in constructing their Tables V and VI. For their own purpose this use was justified for they were employed in computing a small correction term in solutions of relatively low ionic strength and neglect of the factor γ_{HCl}^2 was without significance. The correct interpretation was further clouded by a misprint in equation (12) of MacInnes and Belcher's first paper (ref. 2a) which is, however, given in correct form as equation (3) of their second paper (ref. 2b). The latter equation shows clearly the dependence on γ_{HCl}^2 in relating (K_2) to the stoichiometric constant

$$\left(K_2 \frac{\gamma_{\text{HCO}_3^-}}{\gamma_{\text{H}^+} \gamma_{\text{CO}_3^{2-}}} \right)$$

those of T., W. and F. by as much as 100% in the higher salt concentrations. We employed the same equation used by T., W. and F. to correct for hydrolysis of carbonate ion, namely

$$\frac{x^2}{C-x} = \frac{k_w}{k'_m} \quad (1)$$

with C set equal to *total* carbonate concentration in solution (equal as well to divalent metal ion concentration); x , to the concentration of bicarbonate ion; $(C-x)$ to that of carbonate ion; k_w to the stoichiometric ionization constant of water in the salt solutions and k'_m to the correct stoichiometric second ionization constant of carbonic acid in the solutions. The latter is computed from MacInnes and Belcher's tabulations of pK_2 ² by the relationship

$$\log k'_m = -pK_2 - 2 \log \gamma_{\text{HCl}} \quad (2)$$

In solving equation (1) for x , necessary in the eventual computation of the mean molality of barium (or strontium) and carbonate ions and the evaluation of the activity coefficients of barium (or strontium) carbonate, we employed the following sources of data.

Values of C are taken from Tables I and II of Townley, Whitney and Felsing. These are smoothed values of their solubility measurements in potassium, sodium and lithium chloride solutions, respectively.

The values of k_w are taken from the data of Harned and co-workers⁴ who have determined the

(4) (a) Harned and Hamer, *THIS JOURNAL*, **55**, 2194 (1933); (b) Harned and Copson, *ibid.*, **55**, 2206 (1933); (c) Harned and Mannweiler, *ibid.*, **57**, 1874 (1935); (d) Harned and Cook, *ibid.*, **59**, 2304 (1937).

degree of water dissociation in each of the three chlorides and at, or near, both 25 and 40°.

Values of k'_m were computed, for potassium chloride solutions, by use of equation (2) with pK'_2 taken from the tables of MacInnes and Belcher^{2a,b} and γ_{HCl} from Table IV of Harned and Hamer.^{4a} Interpolations were made by graphical methods. MacInnes and Belcher's measurements at 38° were assumed valid at 40°.

For sodium and lithium chlorides evaluation of k'_m is, of necessity, less exact. Reliable values of γ_{HCl} in these solutions are available^{4b,c} but MacInnes and Belcher's determinations of pK'_2 are limited to potassium chloride solutions and no determinations of similar accuracy are available for sodium and lithium chlorides. We corrected for this as follows

$$k'_m \text{ equals } \left(K_2 \frac{\gamma_{\text{HCO}_3^-}}{\gamma_{\text{H}^+} \gamma_{\text{CO}_3^{2-}}} \right)$$

where K_2 is the true thermodynamic dissociation constant, whence

$$\log (k'_m)_{\text{NaCl}} - \log (k'_m)_{\text{KCl}} = \log \left(\frac{\gamma_{\text{HCO}_3^-}}{\gamma_{\text{H}^+} \gamma_{\text{CO}_3^{2-}}} \right)_{\text{NaCl}} - \log \left(\frac{\gamma_{\text{HCO}_3^-}}{\gamma_{\text{H}^+} \gamma_{\text{CO}_3^{2-}}} \right)_{\text{KCl}}$$

and a similar relationship holds for the ratio of $(k'_m)_{\text{LiCl}}$ to $(k'_m)_{\text{KCl}}$. Further, $\gamma_{\text{CO}_3^{2-}}$ can be set equal to $\gamma_{\text{HCO}_3^-}$ as an approximation.^{5,6} A simi-

(3) This approximation should be quite good at low ionic strengths (to 0.1 or 0.2 μ) where the mean activity coefficient of the alkali bicarbonate should be given rather accurately by an expression of the type

$$\log \gamma_{25^\circ} = \frac{-0.504 \sqrt{\mu}}{1 + A \sqrt{\mu}} \quad (3)$$

[Debye and Hückel, *Physik. Z.*, **24**, 185 (1923)], where A is a constant related to the "mean ion size," and that of the alkali carbonate by the expression

$$\log \gamma_{25^\circ} = \frac{-1.008 \sqrt{\mu}}{1 + A \sqrt{\mu}} \quad (4)$$

Since it is fair to conclude that carbonate and bicarbonate ions will differ little in size (Ref. 6) the A 's can be set equal and it follows that

$$\log \gamma_{\text{M}_2\text{CO}_3} = 2 \log \gamma_{\text{MHCO}_3} \quad (5)$$

and

$$\log \gamma_{\text{CO}_3^{2-}} = 4 \log \gamma_{\text{HCO}_3^-}$$

At ionic strengths above 0.1 or 0.2 the mean activity coefficients of the electrolytes require the addition of a linear term in μ , to correct for the influence of the ions on the dielectric constant of the medium. This leads to equations of the type

$$\log \gamma_{\text{MHCO}_3} = \frac{-0.504 \sqrt{\mu}}{1 + A \sqrt{\mu}} + B_{\text{MHCO}_3} \mu \quad (6)$$

$$\log \gamma_{\text{M}_2\text{CO}_3} = \frac{-1.008 \sqrt{\mu}}{1 + A \sqrt{\mu}} + B_{\text{M}_2\text{CO}_3} \mu \quad (7)$$

[Hückel, *ibid.*, **26**, 93 (1925), also cf. Harned, *THIS JOURNAL*, **48**, 326 (1926), and Åkerlöf, *ibid.*, **48**, 1160 (1926)], whence

$$\log \gamma_{\text{M}_2\text{CO}_3} = 2 \log \gamma_{\text{MHCO}_3} + (B_{\text{M}_2\text{CO}_3} - 2B_{\text{MHCO}_3}) \mu \quad (8)$$

and the extent to which the approximation we use is in error is determined by the magnitude of the term in μ .

Walker, Bray and Johnston (ref. 6) claim to have shown that $\log \gamma_{\text{CO}_3^{2-}} = 4 \log \gamma_{\text{HCO}_3^-}$ for several of the alkali carbonate-bicarbonate mixtures in alkali chloride solutions but the proof that they offer appears rather to confirm only the experimental accuracy of their

lar relationship has held in other solutions of similarly related mono-, di- and trivalent ions.⁷

We may therefore write

$$\log (k'_m)_{\text{NaCl}} = \log (k'_m)_{\text{KCl}} + \log (\gamma_{\text{H}^+} \gamma_{\text{HCO}_3^-})_{\text{KCl}} - \log (\gamma_{\text{H}^+} \gamma_{\text{HCO}_3^-})_{\text{NaCl}}$$

and reduce this to the form

$$\log (k'_m)_{\text{NaCl}} = \log (k'_m)_{\text{KCl}} + 4 \log \frac{(\gamma_{\text{HCO}_3^-})_{\text{KCl}}}{(\gamma_{\text{HCO}_3^-})_{\text{NaCl}}} \quad (11)$$

by the not unreasonable assumption that $(\gamma_{\text{H}^+})_{\text{KCl}}$ bears to $(\gamma_{\text{H}^+})_{\text{NaCl}}$ very nearly the same ratio as $(\gamma_{\text{HCO}_3^-})_{\text{KCl}}$ to $(\gamma_{\text{HCO}_3^-})_{\text{NaCl}}$.

The final term in equation (3) is evaluated from Table XII of Walker, Bray and Johnston,⁶ and is considered to be the same at 25 and at 40°. The influence of this correction alone affects the activity coefficients of the carbonates to the extent of about 10% at the higher ionic strengths in aqueous lithium chloride.⁸

Finally, the values of x obtained from equation (1) were employed to yield values of $(1/m_{\pm})$, by the relationship $m_{\pm} = \sqrt{C(C-x)}$, and a plot was made of $\log (1/m_{\pm})$ vs. $\sqrt{\mu}$ for the several solutions. Extrapolation to $(\mu = 0)$ gave the limiting values listed in Table I.

determinations of ϕ/ϕ_0 (defined as $\gamma_{\text{CO}_3^{2-}}/\gamma_{\text{HCO}_3^-}^2$) arrived at both from equilibrium and cell measurements. However, their data for the potassium salts can be shown to confirm the above simple relationship in the following manner.

Combination of equations (6) and (7) with the definition of (ϕ/ϕ_0) , and the introduction of activity coefficient of the metal ion leads correctly to the result

$$\log \phi/\phi_0 = \frac{-\sqrt{\mu}}{1 + A \sqrt{\mu}} + 4B_{\text{MHCO}_3} \mu + (6B_{\text{M}_2\text{CO}_3} - 12B_{\text{MHCO}_3}) \mu \quad (9)$$

$$= 2 \log \gamma_{\text{MHCO}_3} + (6B_{\text{M}_2\text{CO}_3} - 12B_{\text{MHCO}_3}) \mu \quad (10)$$

Disappearance of the last term in (10) leads to the assumed relationship $\gamma_{\text{M}_2\text{CO}_3} = \gamma_{\text{MHCO}_3}^2$ or $\gamma_{\text{CO}_3^{2-}} = \gamma_{\text{HCO}_3^-}^2$. Walker, Bray and Johnston's data for the potassium salts are quite accurately reproduced by the equation

$$\log \phi/\phi_0 = \frac{-\sqrt{\mu}}{1 + 1.72 \sqrt{\mu}}$$

over the whole concentration range (*i. e.*, to $\mu = 2.5$) which is equivalent to equation (9) with both of the terms in μ removed (*i. e.*, implies that equations (3) and (4) yield the correct activity coefficients for the potassium salts in chloride solutions even to μ greater than 2). A similar experimental simplification does not hold for their measurements on sodium salts which may mean only that B_{MHCO_3} is not negligible in the sodium salt solution. Accurately, this would permit us to use the simplification $\log \gamma_{\text{CO}_3^{2-}} = 4 \log \gamma_{\text{HCO}_3^-}$, with full confidence above $\mu = 0.1$ or 0.2 only within the potassium chloride parentheses of our equation (11). However, it does not appear to us reasonable that sensible error is introduced by using the simplifications for sodium chloride as well.

(6) Walker, Bray and Johnston, *THIS JOURNAL*, **49**, 1235 (1927).

(7) McDowell and Johnston, *ibid.*, **58**, 2009 (1936); Johnston and Leland, *ibid.*, **60**, 1439 (1938).

(8) In the treatment by Townley, Whitney and Felsing this correction for sodium and lithium salt solutions was neglected—*i. e.*, they considered the change of the stoichiometric ionization of water with the variation in salt solutions but not the change in the stoichiometric ionization of carbonic acid.

TABLE I

LIMITING VALUES OF $(1/m_{\pm})$ AT $\mu = 0$		
Carbonate	Temp., °C.	$(1/m_{\pm})_{\mu=0}$
SrCO ₃	25	43,680
SrCO ₃	40	44,170
BaCO ₃	25	22,180
BaCO ₃	40	19,110

Values of $(1/m_{\pm})$ were read from the curve for convenient values of μ and used to obtain γ by the relationship

$$\gamma = \left(\frac{1}{m_{\pm}}\right)_{\mu=m} / \left(\frac{1}{m_{\pm}}\right)_{\mu=0} \quad (12)$$

Values of γ so computed are listed in Tables II and III.

The absolute accuracy of these values is probably not better than $\pm 2\%$, but the relative values for each salt at a given temperature should be somewhat more accurate than this figure, and for this reason the third figure as given in the values of γ is included.

TABLE II

MEAN ACTIVITY COEFFICIENTS OF BARIUM CARBONATE IN AQUEOUS SALT SOLUTIONS

Ionic strength	25°			40°		
	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.001	0.905	0.925	0.936	0.916	0.916	0.919
.002	.863	.893	.909	.881	.879	.885
.005	.780	.835	.855	.814	.807	.819
.01	.685	.760	.795	.737	.727	.744
.02	.555	.663	.711	.627	.615	.637
.03	.460	.585	.649	.543	.535	.557
.04	.391	.524	.600	.478	.474	.497
.05	.342	.473	.558	.421	.420	.455
.07	.275	.398	.491	.357	.363	.403
.10	.214	.326	.415	.293	.302	.355
.15	.161	.253	.335	.227	.244	.304
.20	.131	.210	.283	.186	.208	.269
.30	.100	.161	.219	.138	.167	.230
.50	.075	.115	.176	.094	.120	.194
.70	.064	.070	.158	.070	.110	.174
1.00	.048	.073	.132	.051	.098	.157

TABLE III

MEAN ACTIVITY COEFFICIENTS OF STRONTIUM CARBONATE IN AQUEOUS SALT SOLUTIONS

Ionic strength	25°			40°		
	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.001	0.854	0.913	0.924	0.839	0.918	0.888
.002	.794	.871	.893	.772	.884	.852
.005	.682	.796	.832	.657	.817	.753
.01	.573	.713	.764	.551	.742	.665
.02	.451	.598	.673	.435	.632	.561
.03	.382	.509	.607	.372	.561	.494
.04	.335	.442	.554	.328	.487	.446
.05	.305	.395	.511	.298	.438	.413
.07	.269	.333	.442	.256	.370	.366
.10	.239	.276	.373	.210	.299	.320
.15	.210	.206	.304	.182	.218	.271
.20	.189	.162	.263	.161	.166	.238
.30	.160	.122	.217	.136	.118	.206
.50	.139	.097	.184	.110	.080	.177
.70	.132	.082	.170	.096	.063	.175
1.00	.130	.082	.161	.083	.052	.183

Summary

The mean activity coefficients of barium and strontium carbonates in aqueous solutions of the alkali chlorides, published originally by Townley, Whitney and Felsing,¹ have been recomputed. The recomputations correct for: (1) improper evaluation of the mean molalities; (2) misinterpretation of constants published by MacInnes and Belcher² and (3) differences in the degree of carbonic acid dissociation in the several alkali halides. The latter correction was made with the aid of Walker, Bray and Johnston's³ observations concerning the activity coefficient ratio of carbonate and bicarbonate ions in alkali chloride solutions. The influence of the above corrections affects barium carbonate activity by some 40% at unit ionic strength, and about doubles the values for strontium carbonate.

Tables of the corrected values are given, for 25 and 40°.

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