

Foreword [LH Flint, *Behavior Patterns of Hydration* 1964

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The importance of Lewis Herrick Flint's work on hydration cannot be overstated. It certainly ranks on a par with: the revolutionary works of Aristarchus of Samos, hero of Archimedes and true father of knowledge of our heliocentric universe; Johannes Kepler, whose 3<sup>rd</sup> harmonic law in particular demonstrated with mathematical precision the algebraic structure of our heliocentric universe; possibly Henry G. J. Moseley, whose researches established a precise algebraic relation between atomic numbers and wavelengths of vibration of the various elements; and precious few others. Of course, the world is familiar with the likes of Archimedes, Copernicus, Newton and Einstein, but even aura of these familiar names arguably must acknowledge the primary true importance of Aristarchus, Kepler and Flint within the grand history of science..

As with the earlier giants (indeed what makes them giants), Flint's work is not theoretical; rather, it is calculated from incontrovertible physical phenomena. Flint's work does not provide all the answers to the mysteries of science that remain, but it does provide a framework and solid foundation that seemingly can and will provide the answers (if we don't self-destroy first).

Simply stated, what Flint discovered was a simple algebraic relationship (inverse and integral) that exists between the atomic number (plus valence) of a given ion, and the maximum and commonly-encountered numbers of water units that are associated with it when that ion is dissolved in water. This entity is commonly referred to as the hydration number, or respective hydration numbers, and their identities and underlying behavior remain among the greatest of mysteries of science.

The importance of the relation between water and things dissolved in or combined with it is immediately evident in the indispensable role of water in all of the physical sciences, prominently including chemistry, physics and biology. Thus even from a cursory glance it is clear that a true understanding of the interaction between water units and its varied associates is indeed a grand unifying scientific principle. Conversely, were the object of scientific inquiry to be the discovery of a "grand unification" scheme, the unique and eminently sensible foundation for

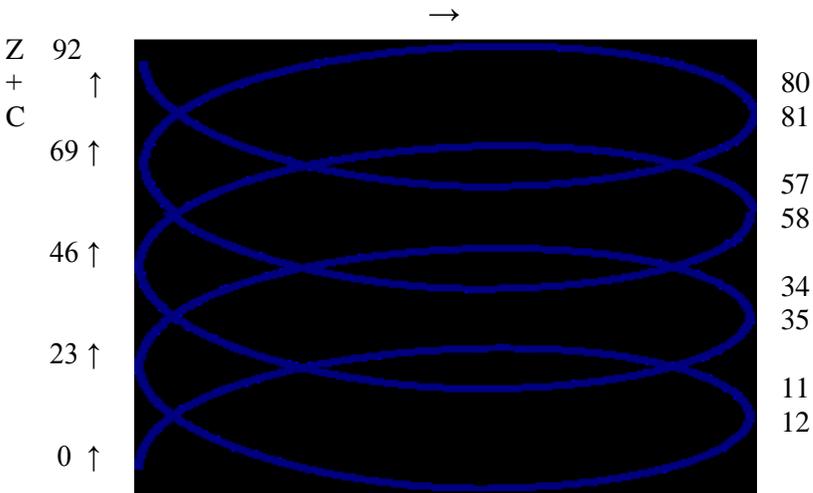
such a scheme would logically be the disclosure of the mechanism of interaction between water units and its associates.

As disclosed by Flint, and more fully discussed in this volume, a subsequent volume (*Hydration and Biology*), and Shakman's *Principles of Hydration*:

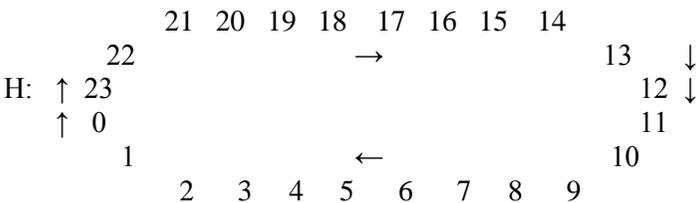
Table 1. Flint's Description of Hydrational Potentiality

H (the (maximum) hydration number) =  $23n - (Z+C)$ ;  
 when Z = atomic number; C = valence; and  
 n=1 for (Z+C)=0-23,  
 n=2 for (Z+C)=23-46,  
 n=3 for (Z+C)=46-69,  
 n=4 for (Z+C)=69-92; and within each of these periods, the maximum hydration number (H) decreases from 23 to zero.

Figure 1. The Helical Structure of Hydrational Periodicity  
 As Z+C increases: 0-23, 23-46, 46-69, 69-92



H decreases from 23 to 0, repetitively.



With the benefit of hindsight, we may illustrate Flint's discovery with direct calculations from well-established non-controversial fundamental data. The data set is comprised of "limiting ionic conductivities", i.e., the relative amounts of electrical current conveyed by the various ions in solution. A tremendous amount of research energy was expended in this area particularly around the turn of centuries, from the 19<sup>th</sup> to the 20<sup>th</sup>. Prominent in these researches are found the great names of science of the era, van't Hoff, Nernst, Arrhenius, Kohlrausch and others, including the particularly exhaustive efforts of Harry Jones of the Carnegie Foundation. In this quest, this particular line of inquiry was indispensably enabled by Kohlrausch, whose law of independent migration of ions enabled conductivities of the individual ions to be separated out from the measured conductance of various solutes (e.g., NaCl, KCl, etc.), and isolated for examination in the form of "limiting ionic conductivities" (e.g., Na<sup>+</sup>, K<sup>+</sup>, etc). At the same time, these values are also known to represent the relative mobilities, or velocities, of the given ions.

The bases for this illustration of direct calculation of hydration numbers, from limiting ionic conductivities, are the same as used by Flint in his discovery. The fundamental principles are (1) van't Hoff's decisive demonstration of the analogy between gaseous (atmospheric pressure) and solute (osmotic pressure) behavior [for which van't Hoff was awarded the first Nobel], and (2) the principle formerly known as Graham's law (now implicit within the law of kinetic energy), whereby gaseous velocity into a vacuum varies inversely with the square-root of the mass – in other words, a gas with 4 times the mass will travel half as fast, with 9 times the mass, 1/3 as fast, etc.

While these two principles were well-established by the time of Flint (1932), it does not appear that anyone prior to Flint had attempted to use these in conjunction with ionic conductivities/ mobilities to attempt to determine relative hydration numbers. While Flint was apparently working from, and adjusting numbers of, Bousfield that were cited in Flint's graduate school Bayliss physiology text (see Flint 1932 and Shakman's *Principles of Hydration* 2014 for further discussion), herein, in Table 2 and Figure 2, is an illustration of Flint's discovery directly

calculated from conductivity data kindly provided through referral in 1996 by Prof. Howard Reiss of UCLA to the then-current textbook, Noggle, J.H., *Physical Chemistry*, 1996, p. 411.

Direct Calculation of Hydration Numbers (This direct calculation method had been proposed but not published, registered as *Nature SXA011*)

There are three steps involved in the calculation of hydration numbers from equivalent ionic conductivities:

- (a) total (relative) ionic weights are derived as the inverse-square of respective conductivities, and adjusted relative to the value of a base ion assumed to be anhydrous;
- (b) weights of anhydrous solutes are subtracted from total ionic weights to derive weights of water of hydration associated with respective ions;
- (c) weights of water of hydration are divided by weight per water unit (18) to derive numbers of water units (hydration number) associated with respective ions.

Equation used in calculations, Table 2 and Figure 2:

$$H_{calc} (\text{calculated Hydration number}) = (k/(\text{conductance}^2) - AW)/18; k (\text{constant in calculations}) = 517336$$

This constant corrects all values relative to an atomic weight of 85.4768 for the “base” ion Rb<sup>+</sup>, which for the purpose of this set of calculations is assumed to be anhydrous, i.e., to have a hydration number of zero.

Figure 2 plots calculated hydration numbers against respective sums of atomic number and valence. The inverse linear result shown in Figure 1 illustrates the essential foundation of the methodology first encountered and discussed by L. H. Flint in 1932<sup>3</sup>, wherein, for the hydrated lighter ions being studied, i.e., Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>, the sums of Z+C+H were found to equal 23.

As shown in Table 2 and Figure 2, calculations for H<sup>+</sup> and OH<sup>-</sup>, as well as the base ion, Rb<sup>+</sup>, also yield approximate linear results at H = 0. The suggestion that relatively large conductivities of H<sup>+</sup> and OH<sup>-</sup> indicated they were not hydrated was first made by Abegg and Bodlander<sup>4</sup> in 1899, first calculated by Flint<sup>3</sup> in 1932 and explained by Flint as evidencing dehydration due to the electrical stress imposed in measuring conductance<sup>5</sup>.

1. Noggle, J.H., *Physical Chemistry*, 1996, p. 411.
2. Gluekauf, E., *Faraday Soc., Transactions* 51 1241 (1955).

3. Flint, L. H., J. Wash. Acad. of Sci. 22, 97-119, 211-217 & 233-237 (1932).
4. Abegg and Bodlander, Zeit. f. Anorg. Chem. 454-499 (1899).
5. Flint, L.H., Dissenting Ape, Dahlia Street, New York, 1973.2

Table 2 / Figure 2: Inverse square of limiting ionic conductance (l) adjusted to base weight of 85.47 for Rb<sup>+</sup>; minus respective atomic weights (A.W.), equals weight of water of hydration, divided by 18 equals calculated hydration number (Hcalc).

Calculated hydration number (Hcalc) from conductance (EC) & atomic weight (AW)

Hcalc= ((k/EC-square)-AW)/18; k=517323 when base is Rb<sup>+</sup> with Hcalc=0.

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ION	Z	C	AW	EC	IW calc	WW	H calc
Rb (BASE)	37	1	85.4678	77.8	85.46781	1E-05	0
H	1	1	1.0078	349.8	4.227875	3.2201	0.1789
OH	9	1	17.0073	197.6	13.24915	-3.758	-0.209
Li	3	1	6.941	38.66	346.1291	339.19	18.844
Na	11	1	22.9898	50.08	206.2686	183.28	1.182
Mg	12	2	24.305	53.06	183.75	159.44	8.8581
Al	13	3	26.9815	63	130.3409	103.36	5.7422
K	19	1	39.0983	73.48	95.81279	56.714	3.1508

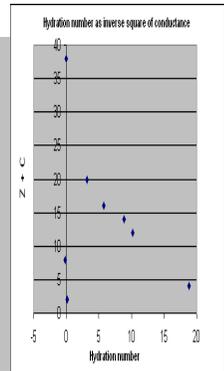


Table 3/ Figure3: The middle (Rb<sup>+</sup>) column of Table 3 duplicates the values for Hcalc in Table 2 for a larger range of ions. The other columns of Table 3 use H<sup>+</sup> and La<sup>3+</sup> as base ions (respectively assumed to be anhydrous, as shown) for comparison:

BASE=	Input-AW (Atomic Wt)		
	H <sup>+</sup>	Rb <sup>+</sup>	La <sup>3+</sup>
OH-	-0.77	-0.21	0.01
H <sup>+</sup>	<b>0</b>	0.17	0.25
Li <sup>+</sup>	4.19	18.84	24.7
Be <sup>++</sup>	2.88	13.69	18.01
Na <sup>+</sup>	1.45	10.18	13.67
Mg <sup>++</sup>	1.08	8.86	11.97
Al <sup>+3</sup>	0.23	5.74	7.95
K <sup>+</sup>	-0.9	3.15	4.77
Rb <sup>+</sup>	-3.62	<b>0</b>	1.45
Cs <sup>+</sup>	-6.24	-2.57	-1.11
La <sup>+3</sup>	-6.31	-1.8	<b>0</b>

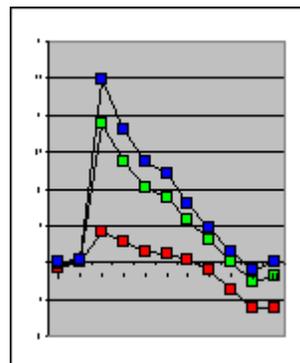


Table 4/ Figure 4: duplicates Table 3 / Figure 3, except for the substitution of Atomic Number (Z) in the place of Atomic Weight (AW):

BASE =	Input-Z (Atomic No.)		
	H+	Rb+	La+3
OH-	-0.59	-0.32	-0.19
H+	<b>0</b>	0.08	0.13
Li+	7.87	14.68	18.23
Be++	5.63	10.69	14.74
Na+	3.77	7.83	9.94
Mg++	3.14	6.75	9.59
Al+3	1.78	4.34	6.31
K+	0.36	2.25	3.23
Rb+	-1.68	<b>0</b>	0.87
Cs+	-3.45	-1.75	-0.87
La+3	-3.18	-1.09	<b>0</b>

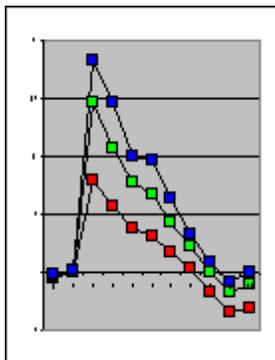


Table 5/ Figure 5: duplicates Table 4 / Figure 4, except for the substitution of Atomic Number plus Valence (Z+C) in the place of Atomic Number (Z):

BASE =	Input-Z (Atomic Number) +C(Valence)		
	H+	Rb+	La+3
OH-	-0.19	-0.23	-0.21
H+	<b>0</b>	-0.01	0.04
Li+	17.73	16.65	21.22
Be++	12.75	11.95	15.33
Na+	9.5	8.86	11.58
Mg++	8.09	7.52	9.95
Al+3	5.07	4.66	6.38
K+	2.81	2.51	3.78
Rb+	0.27	<b>0</b>	1.13
Cs+	-1.67	-1.95	-0.8
La+3	-1.07	-1.41	<b>0</b>

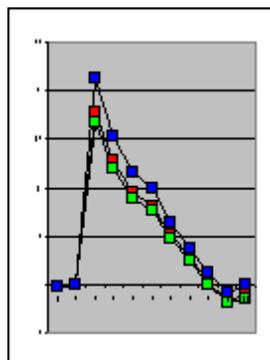


Table 6 / Figure 6 illustrates the concept of periods, based on calculations of hydration numbers from conductance, as proposed by Flint; for the range of ions shown, the totals of Z+C+H tend to cluster around values indicating the first, second or third hydrational period:

ION	Z	C	H	$N=(Z+C+H)/23$
Na=base	11	1	11	1
Li	3	1	20.25	1.054413
Be	4	2	14.61	0.896019
Na (base)	11	1	11	1
Mg	12	2	9.431	1.018753
Al	13	3	6.016	0.957202
K	19	1	3.507	1.022029
Sr	38	2	4.322	1.927055
Y	39	3	3.38	1.973051
N3	21	-1	4.275	1.055424
HS	17	-1	5.543	0.936671
HCO3	31	-1	12.29	1.838563
H2PO2	33	-1	11.06	1.872288
HPO4	48	-2	23.29	3.012739
H2PO4	49	-1	23.07	3.090034
PO4	47	-3	1.608	1.98296
CNO	21	-1	5.19	1.095214
SeCN	47	-1	2.278	2.09905
PO3F	48	-1	2.498	2.152065
PF6	69	-1	1.998	3.04341

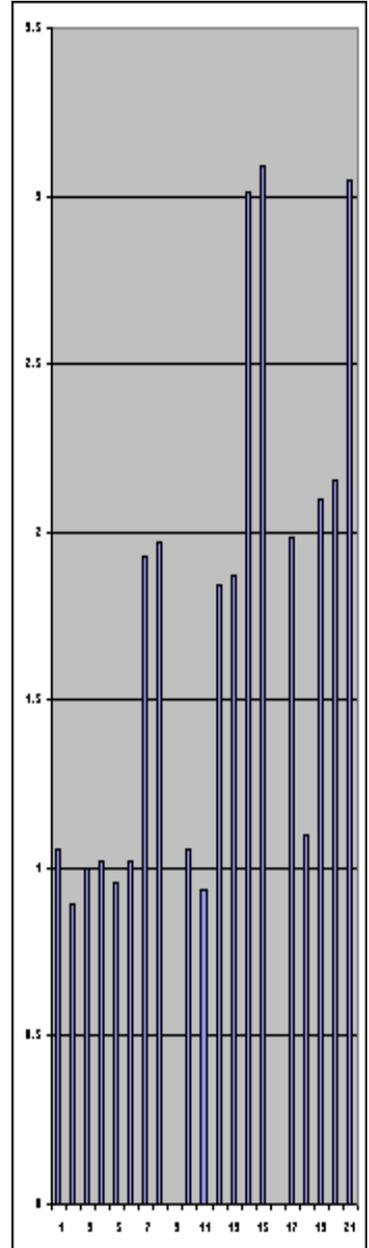


Table 7 below illustrates calculations of both diameters and conductivities for the set of eight ions listed by Ganong.\* For a majority (five) of these eight (hydrated) ions, both diameter\* & conductivity\*\* may be approximated as cube-root of volume & inverse-square-root of weight, respectively when these ions are assumed to be fully hydrated as per Flint\*\*\*.

IONIC SIZE AND CONDUCTIVITY						
Ion		Diameter		Conductivity		
		Obs*	Calc	Ob**	Calc	H
Na+	BASE	1.47	1.47	50.1	50.1	11
K+		1.00	1.02	73.5	76.9	3
HCO <sub>3</sub> <sup>-</sup>		1.65	1.66	44.5	40.0	16
CH <sub>3</sub> COO <sup>-</sup>		1.80	1.68	40.9	40.0	16
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>		2.04	1.84	33	34.3	21
Cl <sup>-</sup>		.96	1.28	76.3	59.4	7
" alt.		.96	1.04	76.3	76.6	3.5 *
HPO <sub>4</sub> <sup>--</sup>		2.58	1.89	33	33.2	23
" alt.		2.58	2.39			*
SO <sub>4</sub> <sup>--</sup>		1.84	1.89	80	33.2	23
" alt.				80	77.8	0 *

\*GANONG, W.F., *Review of Medical Physiology* (1975) 12.

\*\* CRC (1985-6) D167-8.

\*\*\*FLINT, L.H., *Behavior Patterns of Hydration* (1964) 21-30:

Wa[anhydrous weight]=2(atomic # +- valence); Wh[hydrated weight]=Wa+18H; H[hydration#] =23n-(atomic # +-valence) [H=23 to 0, n=1 to 4]; Vh[hydrated volume]=Wh/{1+(Wa/Wh)}.

\* Anomalous results may be improved (alt.) for:

(a) both size and conductivity of the Cl<sup>-</sup> ion by assuming an hydration number [H] of half the prescribed maximum. An hydration number of 3.5 was first suggested by Bousfield, and could represent a type of sharing or bonding;

(b) the diameter of HPO<sub>4</sub><sup>--</sup> by speculatively deriving it as the cube-root of 2 fully-hydrated ionic volumes, while this ion calculates as a single fully-hydrated ion when measured for conductivity. This could be taken to suggest that this ion, when not under electrical stress, may exist in a binary form, as do many gaseous atoms, e.g., H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, etc.; but is split into its two parts when under electrical stress, while each part holds its water of hydration complement.

(c) conductivity of the SO<sub>4</sub><sup>--</sup> ion by assuming it is fully hydrated when measured for diameter, and anhydrous when measured for conductivity. The precise data suggest that the sulfate ion releases all of its water of hydration

under electrical stress, becoming an anhydrous ion. The potential of exploiting such an apparent electrical ionic switching mechanism in biological / medical situations seems worthy of wistful contemplation.

Dr. Flint discusses in depth variations in hydrational status as a result of electrical stress or other conditions, such as hydrational bonding, in his two volumes, usually in a physiological context. The importance of these concepts to animals such as humans is self-evident, for without the likes of hydrational bonding we would collapse in a puddle of mostly water. Beyond this all-encompassing fact, the reality of life's processes being governed by eminently calculable (and presumably thus reversible) osmotic processes presents the exciting prospect of inevitable control of these processes, e.g., even those of disease and aging. The prospect of truly understanding and managing transitions between matter and energy, not merely on the explosive scale of nuclear energy but on the internal living scale, the transition between matter consumed and energy expended in the individual, in a precise and algebraically calculable form, is mind-boggling. But the significance is by no means limited to biology.

The calculations above and further mathematical explorations set out in *Principles of Hydration* are offered as a measure of potential validation, but are not suggested as definitive. Indeed, Flint himself has emphasized that he is outlining and extending his discovered methodology as well as he was able, but that nothing was sacrosanct and beyond improvement. Indeed what we have here is a foundation and framework for further exploration, study, and wherever feasible, implementation.

Flint's laws of hydration are merely a tool for unlocking the mysteries of science, but arguably the most powerful and all-encompassing tool ever encountered. Exposure to this magnificent body of work, and the opportunity to possibly extend it and be a vehicle for helping share it with the world, are certainly among the most thrilling, gratifying and humbling experiences that anyone might enjoy in a precious, brutally short, lifetime.

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