

SCIENCE

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A LUMP OF SALT AND A GLASS OF WATER.¹

WITH ordinary use the powers of eye, ear, smell and touch fail to distinguish between the glass of pure water, and that to which salt has been added. The taste alone gives immediate evidence of the difference. But let us examine more closely, and, first, by chemical tests. Solution of silver nitrate, added to the brine, gives a white, curdy precipitate containing chlorine, a platinum wire would take up enough to impart a yellow color to the Bunsen flame, indicating sodium. Thus two constituents may be separately recognized in the solution by the appropriate tests, where only common salt was added. So, in general, if we wish to detect a salt in solution, we depend upon properties belonging to the basic radical and those belonging to the acid radical; the appropriate tests being separately applied. Such properties are called "additive," since they express the sum of the properties of the constituents. The special use of this term may be clearer on reviewing some electrical properties.

Two kinds of solutions are distinguished by means of the electric current. Absolutely pure water seems to be a non-conductor, while the addition of a salt, acid, or base enables the current to flow, the added body being separated into two parts called ions, which appear at the two electrodes. Such bodies are called electrolytes; and the quantity of electricity passing through the fluid is directly proportional to the quantity of electrolyte decomposed. Many organic bodies are not thus decomposed, their solutions being non-conductors. While the molecule of common salt is believed to contain but two atoms, and sugar contains at least forty-five, yet the former may be separated by the electrical influence in a manner from which the latter is free. The forty-five atoms of the sugar molecule dwell together as a unit, while the two atoms of common salt may part company and enter into new relations, thus presenting a scene of activity and complexity which we should hardly expect from its apparent simplicity.

Let a current pass through a solution of copper sulphate, entering through a copper plate, and passing out at any properly coated form; the copper is carried through the solution with the current, and is deposited as an electro plate coating; while the negative radical slips back to attack the kathode. The quantity of basic and acid radicals thus transferred, under given conditions, depends upon the conductivity of the solution; but to compare solutions of different kinds we should make the concentration proportional to the chemical equivalents. In this way Ostwald has measured the molecular electrical conductivity of many solutions of varying degrees of concentration. The following are a few of his results to the nearest unit for extremely dilute solutions — $\frac{1}{1024}$ normal. The differences are shown in small, bold-face type.

Li Cl, 110	9	Na Cl, 119	23	K Cl, 142
5		5		6
Li NO ₃ , 105	9	Na NO ₃ , 114	22	K NO ₃ , 136
8		7		6
Li ClO ₃ , 97	10	Na ClO ₃ , 107	23	K ClO ₃ , 130

¹ Abstract of the annual address before the Washington Chemical Society, delivered Jan. 28, 1892, by Robt. B. Warder.

The numbers obtained for lithium salts are about 9 less than for the corresponding sodium salts, and these about 23 less than for the potassium salts. Comparing the horizontal lines we find the numbers for chlorides about 5 higher than for nitrates, and these about 7 higher than for chlorates.

To appreciate the full meaning of these differences in the numbers we may again refer to the tests of qualitative analysis. A salt has no single property by which it is recognized, but we depend upon the several properties of basic and acid radicals, which are largely independent of each other. The molecular electrical conductivity is here expressed merely by a number; but do not be repelled by a sense of vagueness. This number expresses motion, — the greater the number the more activity displayed in transfer of electricity. The lithium atom is less active in this way than sodium; and this is true, whatever be the company in which the metal is found. The activity of chlorine is greater than that of the nitric radical, and this greater than the chlorine radical; but the activity of the salt must be viewed as the sum of this property for the components. Each number is clearly the sum of two numbers, one belonging to the basic, the other to the acid, radical. On no other hypothesis can we explain the fact that when we select two basic or two acid radicals the substitution of one radical for the other always results in the same change of the number, no matter what third radical may be combined with these two. In a word, the molecular electrical conductivity is an additive property of salt solutions.

If we leave water and brine in the cold both will freeze; but the brine must be cooled to a lower temperature before freezing begins. The differences between freezing point for solutions and the solvent have been made the subject of many extended researches with special forms of thermometer. Readings are estimated to .01°. The result has been a flood of light upon the molecular weights of substances in liquid form, together with some remarkable differences between salt and sugar, between brine and syrup, or between the two classes of solutions which these represent.

Take three similar barometers, introduce a drop of water into the Torricellian vacuum of the first, and the mercury falls; the water is partly changed to vapor, which exerts a certain pressure on the mercury, and this vapor pressure may be measured by the difference in level. Now put a drop of brine into the second barometer, the mercury falls here also, but to a less extent. The vapor pressure of the brine is less than that of pure water. The process of evaporation or condensation in a current of air affords another means of determining the relative vapor pressure of various solutions. If we now boil water and brine in separate vessels the pressure of vapor equals that of the atmosphere; but, when this point is reached, the brine is hotter than the water, — the boiling point of the former is higher. Thus we have a third method of comparing vapor pressures. This property of solutions, in its quantitative aspect, rivals the freezing point as an avenue to the secrets belonging to our subject, which are yet only partly disclosed. As solution proceeds the denser brine gradually mixes with the water above, until at last the whole fluid would be practically uniform. Various salts will diffuse at different rates. A porous membrane will transmit

the molecules of water more readily than those of a salt. For certain theoretical investigations we may conceive a "half permeable" wall with openings so small that the water alone can penetrate. As a filter separates a solution from the insoluble residue, so the half-permeable wall is to transmit the solvent, while preventing the passage of the dissolved salt. No material has been found fully possessing this ideal property; but theoretical deductions have already been confirmed by experiments with clay cells, the pores being partly closed with a film of insoluble precipitate. If a solution fills such a cell, while fresh water surrounds it, the contents soon show a considerable pressure, which is measured by a manometer. This phenomenon is called "osmotic pressure," and we may have several conceptions of its cause. Either there is an attraction between the unlike molecules in the brine and the fresh water, so that the latter flock in where the salt is imprisoned (as ducks fly to the decoy) until the internal pressure arrests the flow; or the osmotic pressure may be due to the aggregate force of impact of the many moving molecules; this is the view generally taken.

The several properties that have just been considered require numerical expression, but these numbers are wonderfully related to each other and to the doctrine of the conservation of energy. For example, consider the relation of osmotic pressure to vapor pressure. Let a cell with half-permeable wall, connected with a vertical tube be filled with solution, and immersed in a tank of pure water; the whole arrangement being placed under a bell jar in vacuum. Under osmotic pressure the solvent will enter the cell until a certain pressure is reached, as determined by the height of the liquid in the vertical tube. Evaporation will take place at the same time, both from the surface of the solution in the tube and from the solvent in the tank, at their respective levels, until the jar is filled with vapor. A condition of equilibrium will eventually be reached, for otherwise we should have perpetual motion. On the half-permeable walls of the porous cell we have an inward and an outward pressure, whose difference is measured by the height and density of the solution in the vertical tube. On the surface of the two fluids we have a vapor pressure, the difference being measured by the same height and the density of the vapor in the bell jar. The former value is the osmotic pressure, the latter is the diminution of vapor tension caused by adding the solid to the solvent; and these two values stand exactly in the ratio of the densities of solution and vapor. By other thermodynamical considerations a relation is traced between osmotic pressure and the change in freezing point, electrical conductivity, etc.

Important analogies between the physical properties of gasses and those of dissolved bodies are pointed out by van't Hoff; the laws of Boyle, Gay-Lussac, and Avogadro all have their counterparts in the phenomena of osmotic pressure.

First. Boyle's law says that the pressure of a gas is inversely proportional to its volume; that is, that as the quantity of any gas in a given volume is increased or diminished the pressure changes in the same ratio; so, the osmotic pressure of many solutions is found to vary directly as the concentration.

Second. Gay-Lussac's law may be expressed by stating that the gaseous pressure varies directly as the absolute temperature; the same is true of osmotic pressure.

Third. Avogadro's law implies that two gases, at the same temperature, will have equal pressures when the masses of

equal volumes are proportional to the molecular weights. The same is true for osmotic pressures in equivalent solutions of different comparable substances. To calculate the osmotic pressure conceive the solvent to be absent, while the solid occupies the same space as gas; the hypothetical gaseous pressure, as determined by the three fundamental laws, is then equal to the osmotic pressure required. Conversely, to determine the molecular weight of a dissolved body, we may find the osmotic pressure and calculate as for a gas; practically, the depression of freezing point is the physical property usually measured.

In a word, the three fundamental laws of gaseous matter are found to be true of dissolved matter simply by substituting osmotic pressure for gaseous pressure, while even the anomalies and limitations so long recognized in gases and vapors find their counterparts in solutions. Can we find identity of cause when there is almost identity of result? In a gas matter is in a far more dilute condition than in ordinary solids or liquids; the intermolecular spaces are evidently far greater than the space occupied by the molecules themselves. The same is true in a dilute solution of salt, only here the intermolecular space is largely occupied by the water. In both cases, motion is indicated by the phenomena of diffusion. In both cases, each moving molecule is endowed with kinetic energy, and the sum of the vis viva of all the molecules exactly accounts for the laws of pressure. The formulas used to unfold the kinetic theory of gases may be applied without change to a kinetic theory of solutions. In a jar of hydrogen, the molecule darts hither and thither at the rate of a mile a second, asking for no support save other molecules, from which it rebounds. If hydrogen mixes with the denser vapors of paraffin, it will still exert its own pressure upon the walls of the vessel, as though it were alone. Our salt is less ethereal. The molecules are heavier. They move more sluggishly. Very slowly do they rise, as though climbing with painful effort upon an unsteady ladder of water molecules. Yet, with the aid of the half-permeable wall, their pressure is found to be just what it should be on the kinetic theory, if the salt alone occupied the space in absence of water.

Anomalies and limitations have always been mentioned. There is no "perfect" gas, none that exactly fulfils the fundamental laws, but hydrogen, which most nearly agrees with the "ideal gas" in its properties, is not compressed to one-tenth its volume by ten-fold pressure, but occupies a little more than one-tenth volume. Here, the molecules themselves may be considered as incompressible bodies occupying too great a fraction of the whole space to be left entirely out of account. A modification of Bowle's law assumes that the total intermolecular space varies inversely as the pressure. In most gases and vapors, however, the deviation is in the opposite direction. As the molecules approach each other their mutual attraction is manifested, for the volume becomes less than required by Boyle's law. The piston of a Corliss engine, which glides so beautifully to and fro, in obedience to valve and governor, is impelled by the bombardment from an army of vapor molecules, each one following its own impulse almost untrammelled in the go-as-you-please contest; yet some mutual attraction is manifest, for the steam exerts a little less pressure upon the piston than would an ideal gas under like conditions. So, osmotic pressure, instead of increasing directly as the concentration, may increase a little less rapidly. There is a well-known body whose vapor density has long been recognized as abnormal.

Ammonium chloride, when converted into vapor, is found

to occupy twice the volume predicted by theory, — in other words a given volume of the vapor exerts twice the theoretical pressure. The explanation is easy when we learn that the salt is dissociated into the two gases, ammonia and hydro-chlorine acid. Similar anomalies in osmotic pressure may lead to a similar interpretation, although quite antagonistic to our ordinary conceptions and teachings. Sodium will burn in chlorine with striking evolutions of light and heat; we recognize the product as a new substance. Chemical action has taken place. By a large expenditure of energy the elements may again be separated; this also is chemical action. But we dissolve the salt in water, evaporate, recover it as before, and are prone to count all these changes as purely physical. Little do we suspect that the dilute solution contains in free state the two substances which we usually know as metal and gas, the two kinds of atoms moving independently of each other, so long as they are distributed in equal numbers in any portion of the fluid. Yet such is the theory of Arrhenius, now fast gaining ground. Cold water decomposes a most stable compound, the elements being gradually reunited in evaporation and crystallization. Accept this hypothesis for electrolytes and their peculiar properties are explained, their additive character must follow as a necessary consequence of their nature, and the several kinds of anomalies fall into harmonious relations.

On this hypothesis the speed of chemical change should no longer be proportioned to the whole quantity of each active substance present, but rather in proportion to that part which has already suffered loosening of the bonds. The facts of dynamical chemistry afford an independent and valuable confirmation of the new views.

THE ORIGIN OF THE ASS, THE CAT, AND THE SHEEP IN CHINA.¹

At a recent meeting of the China Branch of the Royal Asiatic Society in Shanghai, Dr. Macgowan, a well-known Chinese scholar, read a paper on the probable foreign origin of the ass, the cat, and the sheep in China. He said that the Chinese, in their numerical co-ordination of concrete and abstract nature, give the "six domestic animals" as the horse, ox, goat, pig, dog, and fowl; which seems to indicate that when that formula was framed, neither cat, sheep, nor ass had been domesticated there. When familiar beasts were selected to denote years of the duodenary cycle, to the "six domestic animals" were added the rat, tiger, hare, dragon, serpent, and monkey, to complete the dozen, as if the ass, sheep, and cat were too little known to meet the object in view, which was the employment of the most familiar representations of animated nature for the duodenary nomenclature. Still more striking is the absence of the ass, sheep, and cat from the twenty-eight zodiacal constellations, which are represented by the best-known animals.

With regard to the ass, there is ample reason to regard it as being excluded from the list of domestic animals because it was not archaic. The hybrid mule is of comparatively modern origin in China, dating back only about a score of centuries. A miscellany of the Sung era states that "the mule was not seen during the Hsai, Shang, and Chou dynasties; that it was a cross between the ass and horse from Mongolia. It is regularly bred in the north, and is worth in the market twice as much as the horse; it is popularly reported that its bones are marrowless, which is the reason of its inability to produce its kind." Again, it is recorded in a Ming

¹ From Nature.

cyclopædia: "The mule is stronger than the horse, and is not a natural product of China; in the Han era it was regarded as a remarkable domestic animal." Is it likely that, if the ass existed during the three ancient dynasties, there was no crossing with the horse?

With regard to the cat, Dr. Macgowan proceeded to state that there was a quotation from a standard work which discloses the fact that Yuang Chuang, the pilgrim monk, who, in the seventh century A.D., returned after sixteen years' wanderings in India, brought cats with him to protect his collection of Sanscrit Buddhist books from rats. That account, however, is somewhat invalidated by an anecdote of Confucius, who is related to have one day seen a cat chasing a rat. These conflicting statements are from authoritative sources, and it is impossible to offer a satisfactory explanation. Possibly the cat of Confucian times was only a partially domesticated wild cat. There must have been some ground for the statement of the cat having been brought from India, as it is hardly likely that in all the long period of Chinese history it should be named but twice as a domestic animal. He quotes from Chinese folk-lore on the subject of cats. As cruelty to cats and other animals is followed by retribution, so services rendered to them meet with supernal recognition. As anciently the tiger was sacrificed to because it destroyed wild boars, so the wild cat was worshipped because it was the natural foe of rats; boars and rats being the natural enemies of husbandry. At the commencement of the Sui dynasty, A.D. 581, the cat spirit inspired greater terror than the fox did subsequently. The hallucinations of cat spirit mania prevailed, forming a remarkable episode in Chinese history, only to be likened to the fanatical delusion of witchcraft that frenzied Europe a thousand years later. It was believed that the spirit of a cat possessed the power of conjuring away property from one person to another, and inflicted through incantations bodily harm. The popular belief was intensified and spread like an epidemic, until every disastrous affair that took place was ascribed to cat spirit agency set in motion by some mischievous enemy. Accusations were lodged against suspected persons, and, the slightest evidence sufficing for conviction, the malicious were encouraged to trump up charges against the innocent, until the country became a pandemonium. No one was safe, from the Imperial family down to the humble clodhopper. Even a magnate of the reigning house, who enjoyed the titular distinction of Prince or King of Szechuan, was executed for nefariously employing the agency of cat spirits. In this manner several thousands were immolated before the delusion was dispelled. Happily the period appears to have been of brief duration: incentives such as kept up the witch mania for centuries were wanting in China. Coming down to our own times we find a cat-craft delusion prevailed over a great portion of Chêkiang. "In the summer and autumn of 1847 frightful wraiths appeared throughout the departments of Hangchow, Shaohsing, Ningpo, and Taichow. They were demons and three-legged cats. On the approach of night a foetid odor was perceptible in the air, when dwellings were entered by something by which people were bewitched, causing alarm everywhere. On detecting the effluvium in the air, householders commenced gong-beating, and the sprites, frightened by the sonorous noise, quickly retreated. This lasted for several months, when the weird phenomena ceased." Well did he remember, said Dr. Macgowan, the commotion that prevailed in Ningpo throughout those months of terror. Every gong that could be procured or manufactured for the occasion was subject to vigorous thumping