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## NOTE ON COMPUTING DIFFUSION.

By GEO. F. BECKER.

ART. XXV. — *Note on Computing Diffusion*; by GEO. F. BECKER.

DIFFUSIVE phenomena have become of great importance to geologists. As every one knows, Lord Kelvin's famous inquiry into the age of the earth is based on the diffusion of heat in a cooling globe of large radius. The modern theory of the differentiation of rock magmas also is founded on phenomena of molecular flow, the least complex of which is the simplest case of liquid diffusion. The diffusion of motion in a viscous fluid is subject to the same laws and is capable of geological applications. Possibly even the diffusion of current density in a homogeneous conductor may eventually be made to contribute to a knowledge of the earth's interior.

The computation of the simplest diffusive phenomena has a formidable appearance to most geologists, while to those who are mathematically inclined the reckoning appears inelegant and clumsy. It is probable that every one who has actually computed diffusions has seen how the subject could be simplified, but each appears to have shrunk from the trouble of setting the matter straight. I shall attempt to make the subject so easy that no geologist will hesitate to compute any case which may help him to frame a theory or to test an hypothesis.

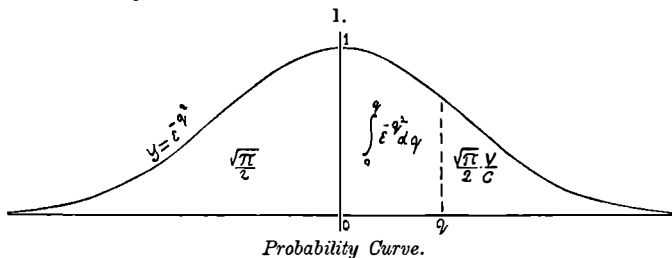
In "linear" motion as defined by Fourier the subject of motion, or the "quality" as Lord Kelvin calls it, varies only in one direction; in other words, it remains uniform at all points in any one plane at right angles to this direction. Qualities in this sense are for example the temperature of a body, the amount of substance in solution per unit volume, the velocity of a viscous fluid. For qualities obeying the law of diffusion the differential equation is

$$\frac{dv}{dt} = \kappa \frac{d^2v}{dx^2}.$$

Here  $v$  is the quality,  $t$  the time,  $x$  the distance from the plane of contact between the subject of diffusion and the medium into which it diffuses, and  $\kappa$  is the "diffusivity" assumed to be constant. The equation may be expressed by the statement that the time rate of change of quality is proportional to the space rate of the space rate of change of quality. It is usual with English writers to apply the C. G. S. system to these measurements. That system attains a most convenient uniformity, though only at the expense of some very awkward numbers.

The simplest case of linear diffusion arises when the diffusing quality at the initial plane is kept constant and when the

space into which it diffuses may be regarded as infinite. The quality at any distance measured perpendicularly to the initial plane is then proportional to the area of the "probability curve" taken between certain limits. Now this area between any limits has repeatedly been computed and tabulated, because it is of importance in the astronomical discussion of refraction, in the theory of probabilities, etc. Thus it is only needful to apply these tables to find the distribution of quality at any time or for any distance.



For this simplest case of diffusion let  $c$  be the initial concentration and let also

$$q = \frac{x}{2\sqrt{\kappa t}};$$

then the quality  $v$  in terms of the initial concentration is simply\*

$$\frac{v}{c} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-q^2} dq.$$

Here  $q$  appears as the abscissa of the probability curve. The value of the integral in this expression has been tabulated, but more usually it is the area from zero to  $q$  instead of that from  $q$  to infinity which is computed. That is a mere matter of detail; for the whole area from zero to infinity is simply  $\sqrt{\pi}/2$ , so that a knowledge of either part of the area leads immediately to the determination of the other. If the accessible tables have the usual form, it is only necessary to write the equation as follows:—

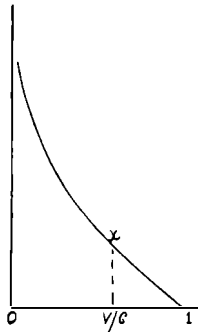
$$\frac{v}{c} = 1 - \frac{2}{\sqrt{\pi}} \int_0^q e^{-q^2} dq.$$

There is thus no mystery or difficulty about computing diffusion when  $\kappa$  is known. Of the three quantities  $x$ ,  $t$ , and  $v$ ,

\* The truth of this theorem is easily tested; but its proof does not come within the scope of this note.

any two may be assumed and the corresponding value of the third found. The practical awkwardness of the results is a consequence of the fact that the tabulations are made with  $q$  for an argument. Hence, the least laborious method is to assume  $q$  at some tabulated even value, find  $x$  or  $t$  from the

2.



Diffusion Curve.

first of the above equations and  $v$  from the second. Thus assuming  $t = 86400$  seconds (one day) and  $\kappa = \cdot 00001$ , which is about the value for common salt, and taking  $q = \cdot 4$ , one finds  $x = 0\cdot 7436$  and by the help of the tables of the integral,  $v = 0\cdot 5716 c$ . A series of corresponding values thus obtained for  $v$  and  $x$  is not easily grasped numerically. On the other hand, these values are readily plotted. It is apparently for this reason that Lord Kelvin has on various occasions represented diffusion by diagrams. Messrs. King and Barus used the same device, and the system of curves by the aid of which Lord Kelvin proposed the computation of diffusions\* is mainly useful for the same reason.

The abscissa of the probability curve is not the natural independent variable for calculating diffusions. Greatly preferable is the quality,  $v/c$ . It is entirely possible to employ it in this way even with the tables hitherto published. The tables of the integral can be entered with rounded values of  $v$ , and corresponding values of  $q$ , containing as many significant places as desirable, can then be interpolated. From such values of  $q$  one can obtain  $x$  and the result is a table showing the distances for rational values of the quality. This, however, is a tedious process, since, for a satisfactory degree of accuracy, the interpolation must be made by second differences.

What is needed to facilitate computation of diffusions in a neat form, such as will not require diagrams to render the relations clear, is a table in which  $q$ , or better  $2q$ , is expressed

\* Rep. Brit. Assoc., 1888, p. 571.

in terms of  $v/c$ . Such a table is given below, but only in skeleton for intervals of  $v/c$  of .05. It will, I think, suffice for the needs of geologists, and it is hardly worth while to extend it to single hundredths unless some desire for such an extension should be manifested.\* Knowing  $2q$  for a stated value of  $v/c$  the value of  $x$  in centimeters follows easily from the equation,

$$x = 2q\sqrt{\kappa t}$$

To find the distance at which any chosen quality exists in linear diffusion after the lapse of  $t$  seconds, it is now only necessary to add half the logarithm of  $\kappa t$  to  $\log 2q$  and take the number corresponding to the sum from a table of common logarithms. This is a labor from which no geologist interested in diffusion can shrink.

The values of  $2q$  are given in part because they are the distances in centimeters after the lapse of one particular time, that, namely, which is the reciprocal of the diffusivity. Thus in the case of salt with a diffusivity of .00001, after a lapse of 100,000 seconds, or some 28 hours,  $\kappa t = 1$  and  $2q$  represents the distances answering to  $v/c$ .

If one is not anxious to preserve the severe simplicity of the C. G. S. system, the day or the year is a more convenient time unit than the second for computing diffusions of liquids as well as of heat in large masses of matter such as the earth. I have therefore tabulated  $\delta$  as defined by the expression

$$x = 2q\sqrt{86400} \cdot \sqrt{\kappa\Delta} = \delta\sqrt{\kappa\Delta},$$

where  $\Delta$  is the time expressed in days; and also  $\gamma$  in

$$x = \delta\sqrt{365 \cdot 24 \cdot 92} \sqrt{\kappa\Gamma} = \gamma \sqrt{\kappa\Gamma}$$

where  $\Gamma$  is the time expressed in years. To make the logarithms of  $2q$  useful in this connection it may be noted that

$$\log \delta = \log 2q + 2.46826; \quad \log \gamma = \log 2q + 3.74955.$$

In German papers it is usual to state the diffusivities of liquids in terms of days, so that if  $\lambda$  is the diffusivity thus stated  $\lambda = 86400 \kappa$  and

$$x = 2q \sqrt{\lambda\Delta},$$

Of course the tabulated values of  $\delta$  answer to a period for

\*The values of  $q$  were computed from the seven-place table of the integral given by Lord Kelvin, Phys and Math. Papers, vol. iii, 1890, p. 434. The interpolations were made by a known formula of the same order of accuracy as the formula for second differences, and the results were tested by substitution in the formula for second differences. Seven-place logarithms were used. The abbreviation to five places introduces an apparent inaccuracy, inasmuch as the  $\log 2q$ , as tabulated, sometimes varies in the last place from the five-place  $\log$  of the tabulated value of  $2q$ . The tabulated logarithms are, however, the nearest in five places to the values of  $2q$  expressed in seven places.

which  $\Delta = 1/\kappa$ , or in the case of salt a period of 100,000 days, while the values for  $\gamma$  correspond for salt to a lapse of time of 100,000 years.

In connection with this table it may be convenient to set down a few diffusivities interesting to the geologist, either immediately, or for comparison with the diffusivity of rock magmas. The data for the diffusion of heat and motion are taken from Lord Kelvin's memoir on Heat. The diffusivities of solutions were all originally published in terms of days, not seconds. In the list below they are stated both in this way under  $\lambda$  and in seconds under  $\kappa$ . In choosing illustrations from the many experiments of Scheffer and of Schuhmeister\* I have when practicable selected two nearly at the same temperature with different concentrations, and a third at a different temperature but with concentration as nearly as may be equal to that of one or other of the first two. There seems no doubt that  $\kappa$  in the case of liquids varies both with concentration and temperature. The variations of  $\kappa$  however, are far from complete elucidation.

Mr. Schuhmeister remarks that "the rapidity of diffusion runs almost exactly parallel with the larger or smaller values of the coefficient of friction," but makes no further comment on the relations of viscosity to diffusivity. In an investigation undertaken by Mr. A. Sprung† in Prof. Wiedemann's laboratory, for the purpose of determining the viscosity of salt solutions over wide ranges of temperature and concentration, diagrams and tables are given which enable one to fix the viscosities of seven salts of which Mr. Schuhmeister has determined the diffusivities for the same temperature and for nearly the same concentration. Sprung's concentrations are given in terms of the weight of anhydrous salt per 100 parts by weight of solution. Schuhmeister's data are for weight of anhydrous salt per unit volume of solution. The concentrations being 1/10 and the temperature 10° C.,  $\kappa$  the diffusivity, and  $\mu$  the coefficient of viscosity, the results of the two observers are expressed in the first three lines of the following little table.

Salt	KBr	KI	KCl	NaCl	CaCl <sup>2</sup>	Na <sup>2</sup> SO <sup>4</sup>	MgSO <sup>4</sup>
$\kappa \times 10^6$	13.08	12.96	12.73	9.72	7.87	7.64	3.24
$\mu$	0.126	0.124	0.128	0.156	0.169	0.179	0.247
$\kappa\mu^2 \times 10^6$	0.207	0.199	0.208	0.236	0.224	0.244	0.198

\* Mr. J. Schuhmeister's investigation, undertaken at Prof. J. Stefan's advice, appeared in *Wieu. Sitz. Ber. Ak. Wiss.*, vol. lxxix, 1879, Part II, p. 603. At the close of the paper mean values of  $\lambda$  are given for 10° C. Stefan recomputed Graham's diffusion experiments. His paper is in the same volume as Schuhmeister's, p. 161. Mr. J. D. R. Scheffer's memoir on diffusion is published in *Verh. Kon. Ak. van Wet.*, xxvi, Part, 1888, with separate pagination.

† *Pogg. Ann.*, vol. clix, 1876, page 1.

In the last line I have shown the product  $\kappa\mu^2$ , which evidently varies slowly and irregularly. Expressed in two figures the average of the two sulphates gives 0.22; the average of the three chlorides gives 0.22; the average of the five alkaline salts gives 0.22; the average for the seven compounds is 0.22. The average for the three potassium salts on the other hand is only 0.20, and the average for the two sodium salts is 0.24.

The variation of  $\kappa\mu^2$  from a single value is perhaps not greater than might be expected from the data on diffusivity (which, as Mr. Schuhmeister himself points out, accord only approximately) if  $\kappa\mu^2$  were really a constant. It is clear that the hypothesis—diffusivity is inversely proportional to the square of the viscosity for uniform temperature and concentration, expresses approximately the facts for these seven compounds. The number of compounds is small, but it embraces salts of four bases and of four acids showing rather a wide range of diffusivities and of viscosities. The probability that the accord is a mere coincidence seems to me extremely slight, and I infer that the hypothesis just stated probably expresses, at least roughly, the relations of diffusivity to viscosity for an important class of compounds. Should it prove that solutions such as rock magmas are to be included in this class, it would greatly facilitate the discussion of rock differentiation. Some approach to a quantitative determination of the viscosity of lavas might be attained. Direct investigation of their diffusivity would seem impossible.

## Liquids diffusing into water.

Solution of	Temp.	Concentration.	$\lambda$	$\kappa$	Authority.
Chlorhydric acid,	11.°	1HCl/7.17H <sup>2</sup> O	2.671	.000 030 91	} Scheffer.
"	11.°	1HCl/108.4H <sup>2</sup> O	1.837	.000 021 26	
"	0.°	1HCl/6.86H <sup>2</sup> O	2.080	.000 024 07	
Sulphuric acid,	7.5.°	1H <sup>2</sup> SO <sup>4</sup> /686.7H <sup>2</sup> O	1.042	.000 012 06	
"	8.°	1H <sup>2</sup> SO <sup>4</sup> /36.2H <sup>2</sup> O	1.008	.000 011 67	
"	13.°	1H <sup>2</sup> SO <sup>4</sup> /35.4H <sup>2</sup> O	1.244	.000 014 40	
Sodium chloride,	7.7.°	.147 85 g. per cm <sup>3</sup>	.810	.000 009 38	
"	8.3.°	.322 38 "	.798	.000 009 24	
"	14.°	.139 75 "	.9015	.000 010 43	
" (Mean),	10.°	.10 "	.840	.000 009 72	
Sodium carbonate,	5.5.°	.099 86 "	.319	.000 003 69	} Schuhmeister.
"	9.5.°	.134 03 "	.375	.000 004 34	
"	20.5.°	.182 42 "	.613	.000 007 10	
" (Mean),	10.°	.13 "	.390	.000 004 51	
Sodium sulphate,	5.3.°	.046 19 "	.614	.000 007 11	
"	10.7.°	.073 24 "	.678	.000 007 85	
" (Mean),	10.°	.10 "	.660	.000 007 63	
Copper sulphate,	8.1.°	.177 64 "	.212	.000 002 45	
"	8.1.°	.088 57 "	.230	.000 002 66	
"	4.6.°	.129 26 "	.203	.000 002 35	
" (Mean),	10.°	.10 "	.210	.000 002 43	
Magnesium sulphate,	4.5.°	.244 05 "	.209	.000 002 42	
"	9.4.°	.309 92 "	.279	.000 003 23	
"	12.7.°	.311 56 "	.305	.000 003 53	
" (Mean),	10.°	.10 "	.280	.000 003 24	
Cane sugar,	10.°	10 per cent	.456	.000 005 28	} Graham; Stefan.
Caramel,	10.°-11.°	10 per cent	.047	.000 000 54	

*Diffusion of heat and motion in C. G. S. units.*

Subject of Diffusion.	Medium.	$\kappa$	Authority.
Heat,	Iron.	.225	Angstrom and Tait.
"	Sandstone,	.023 11	Forbes and W. Thomson.
"	Trachyte,	.010 28	Ayrton and Perry.
"	Trap,	.007 86	Forbes and W. Thomson.
"	Average of rock,	.01	" "
Laminar motion,	Air,	.053	Stokes and Maxwell.
"	Water at 10° C.,	.013 2	Poiseuille, Stokes.

*Diffusion Table, giving distances in terms of quality,  $v/c$ , after the lapse of  $1/\kappa$  seconds, days or years.*

$v/c$	log. $2q$ .	$2q$ in cm.	$\delta$ in cm.	$\gamma$ in cm.
0.0	$+\infty$	$\infty$	$\infty$	$\infty$
.005	0.59876	3.9697	1166.9	22300.
.01	0.56143	3.6428	1070.8	20464.
.05	0.44276	2.7718	814.74	15571.
.10	0.36664	2.3262	683.75	13067.
.15	0.30874	2.0358	598.40	11436.
.20	0.25825	1.8124	532.73	10181.
.25	0.21134	1.6268	478.19	9138.9
.30	0.16606	1.4657	430.84	8233.9
.35	0.12114	1.3217	388.50	7424.8
.40	0.07563	1.1902	349.85	6686.2
.45	0.02870	1.0683	314.02	6001.3
.50	9.97949—10	.95387	280.38	5358.4
.55	9.92704	.84536	248.48	4748.9
.60	9.87018	.74161	217.99	4166.1
.65	9.80734	.64172	188.63	3604.9
.70	9.73634	.54493	160.17	3061.2
.75	9.65381	.45062	132.46	2531.4
.80	9.55431	.35835	105.33	2013.1
.85	9.42725	.26745	78.615	1502.4
.90	9.24972	.17771	52.236	998.31
.95	8.94783—10	.08868	26.067	498.17
1.	$-\infty$	0.	0.	0.

Washington, D. C., February, 1897.