TABLE I.
Latent heat of Fusion in gram calories per 1 gram of metal.

Metal	Latent heat of fusion	Author	Largest difference in percentages
Potassium	15.7	JOANNIS [1]	16
	13.61	BERNINI [2]	
Lead	5.86	RUDBERG [3]	20
	5.37	PERSON [4]	
	5.37	MAZZOTTO [5]	
	5.32	SPRING [6]	
	6.45	ROBERTSON [7]	
Sodium	31.7	JOANNIS [1]	80
	17.75	BERNINI [2]	
	27.5	EZER GRIFFITHS [8]	
Tin (white)	13.3	RUDBERG [3]	10
	14.25	PERSON [4]	
	14.65	SPRING [6]	
	13.6	MAZZOTTO [5]	
	14.05	ROBERTSON [7]	

Utrecht, March 1915.   VAN 'T HOFF-*Laboratory*.

Physics. — *"On the Kinetic Interpretation of the Osmotic Pressure."* By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

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The fact that the dissolved molecules of a diluted solution exert on a semi-permeable membrane in spite of the presence of the solvent exactly the same pressure as if they alone were present and that in the ideal gas state — this fact is so startling that attempts have

[1] Ann. de chim. et de phys. (6) **12**, 381 (1887).
[2] Nuov. Cim. (5) **10**, 1 (1905); Physik. Zeitschr. **7**, 168 (1906).
[3] Pogg. Ann. **19**, 133 (1830).
[4] Ann. de chim. et de phys. (3) **24**, 129 (1848).
[5] Mem. Ist. Lombardo **16**, 1 (1891).
[6] Bulletin Acad. Roy. de Belg. (3) **11**, 400 (1886).
[7] Journ. chem. Soc. **81**, 1233 (1902).
[8] Proc. Roy. Soc. London **89**, (A) 119, (1914).

been repeatedly made to get a kinetic interpretation that was as lucid as possible. With regard to its contents the following discussion is closely connected with the well-known work of L. Boltzmann[1], H. A. Lorentz[2], O. Stern[3], G. Jäger[4], and particularly that of P. Langevin[5][6]. By making use of the virial thesis and of the remarkable property which is further on formulated by equation (1), it is, however, possible to simplify the derivation.

Let in an infinitely extended mass of water through a closed surface Ω a region G of the volume V be distinguished by the following definition: let inside Ω besides the water molecules (W) also n sugar molecules $(S_1 \ldots S_h \ldots S_n)$ be present, outside it only watermolecules. The surface Ω may possess the following properties (of a "semi-permeable membrane"): whenever the centre of gravity of a molecule S is about to pass through Ω, the molecule is perfectly elastically reflected by Ω; Ω does not exert any forces on the molecules W, however. We want to know the pressure P (osmotic pressure), which Ω experiences per cm² through the collisions of the sugar molecules.

Clausius' *virial thesis*, applied only to the sugar molecules, requires that:

$$2\overline{L} + \Sigma_h\overline{(X_hx_h + Y_hy_h + Z_hz_h)} = 0 \quad \ldots \quad (A)$$

Here

x_h, y_h, z_h are the coordinates of the centre of gravity of the hth sugar molecule at an arbitrary moment t;

X_h, Y_h, Z_h are the resultants[7] of all forces acting at the moment t on the hth sugar molecule;

L the kinetic energy of the translation of all the molecules S added together at the moment t.

The horizontal line expresses: taking a mean of a very long time θ.

Let us now follow the hth molecule S during the time θ. The force X_h, Y_h, Z_h on the hth molecule is owing to three causes:

1. to the collisions on the surface $\Omega \rightarrow X_h', Y_h', Z_h'$;

2. to the attraction and repulsion by all the other molecules $S \rightarrow X_h'', Y_h'', Z_h''$;

[1] L. Boltzmann, Z f. ph. Ch. 6 (1890) 474; 7 (1891) 88. [Wiss. Abh. N⁰. 93, 94].

[2] H. A. Lorentz, Z, f. ph. Ch. 7 (1891) 36. [Abhandl. I, p. 175].

[3] O. Stern, Z. f. ph. Ch. 81 (1912) 441.

[4] G. Jäger, Ann. de Phys. 41 (1913) 854.

[5] P. Langevin, Journ. Ch. phys. 10 (1912) 524; 527.

[6] Cf. also Ph. Kohnstamm, These Proc. 7, 729.

[7] We suppose for the sake of simplicity that the molecules are centres of force of one dimension.

3. to the attraction and repulsion by all the molecules $W \rightarrow X_h'''$, Y_h''', Z_h'''.

During the greater part of θ the hth molecule S is found in volume elements far inside the region G, and only during a very small part of θ in the periferic volume elements of G close to the surface Ω. Let us now first direct our attention to a volume element $dx\,dy\,dz$ far in the interior of the region G, far from Ω. Repeatedly the molecule S_h is found for a short time in this element.

In this we find that:

$$X_h'' + X_h''',\ Y_h'' + Y_h''',\ Z_h'' + Z_h'''$$

assumes now positive, now negative values of rapidly varying amount, and — because we are far from Ω, in the midst of the homogeneous solution — equally frequently equally large positive as negative values. Because besides X_h', Y_h', Z_h' are always zero, it is clear that the mean contribution to the virial yielded by the hth molecule S, i. e. S_h, during its residence in an "internal" volume element $dx\,dy\,dz$ of the region G, is :

$$dx\,dy\,dz\,[x\,\overline{X}_h + y\,\overline{Y}_h + z\,\overline{Z}_h] = 0 \quad . \quad . \quad . \quad . \quad (1)\,{}^1)$$

and likewise for every "internal" volume-element. This is no longer the case for "peripheric" volume elements close to the surface Ω. Here in the direction of the normal to Ω the symmetry is disturbed:

1. The force exerted at the impact by Ω on the molecule S_h is always directed inward ;

2. The joint molecules S, which act on S_h all lie on óne side of Ω (the inside);

3. On account of the presence of the molecules S the concentration of the water on the inside of Ω is different from that on the other side.

Let us now add the contributions yielded by *all* the molecules S during their presence in all the "peripheric" volume elements to the second term of the equation (A): Thus we get corresponding to the above mentioned three kinds of forces an expression with three terms :

$$\sum_h (X_h\,x_h + Y_h\,y_h + Z_h\,z_h) = W' + W'' + W''' \quad . \quad . \quad . \quad (2)$$

If the concentration C_s of the molecules decreases to zero, W' becomes small of the same order of magnitude as C_s, on the other hand W'' and W''' of higher order.

${}^1)$ We draw attention to the fact, that this holds as well for repulsive as for attractive forces.

It should be namely borne in mind that:

First of all all the three W's become smaller already on account of this that in (2) the $\sum_i$ must be taken over a number of molecules S, which decreases in direct ratio with c_s.

Secondly, however, W'' decreases *besides* on account of this that the forces X_h'', Y_h'', Z_h'' which a certain molecule S experiences from all the other molecules S, decreases at the same time with the number of the latter to zero, likewise W''', because the *difference* of the concentrations of the molecules W on the two sides of Ω, which determines $x\overline{X'''}$, $y\overline{Y'''}$, $z\overline{Z'''}$, decreases to zero at the same time with c_s. For W', which arises from the collisions of the molecules S with Ω, there does not exist an analogous *second* reason to approach zero.

If therefore in the case of *diluted* solutions we confine ourselves in equation (A) to terms of the first order in c_s, we have:

$$2\,L + W' = 0. \qquad (A')$$

One can now easily convince oneself that this expresses that the dissolved molecules S exert on Ω the same pressure as when they were only enclosed in Ω and that as an ideal gas. W' can namely be calculated from the pressure P exerted by Ω on the sugar molecules, and becomes:

$$w' = -3\,PV \qquad (3)\,{}^{1)}$$

Further:

$$2\,L = 2.3\,n\,aT \qquad (4)$$

when aT is the mean kinetic energy per degree of freedom.

If we take particularly one gramme molecule of sugar, i.e. n equal to the Avogadro value N, and put

$$N\,2\,aT = RT \qquad (5)$$

(A') passes into:

$$PV = RT \qquad (6)$$

V$_{AN}$ 't Hoff's equation for the osmotic pressure of a dilute solution.

The deviations from equation (6) for solutions which are no longer exceedingly diluted, have been repeatedly treated *thermodynamically*. [2] O. Stern has tried to give a purely kinetic treatment in analogy with the kinetic theory of non-ideal gases. [3] Compare also

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[1] Comp. the perfectly analogous calculation for ideal gases L. Boltzmann. Gastheorie II, p. 143, § 50.

[2] Van Laar: Z. f. phys. Ch. 15 (1894) 457; "6 Vorträge" (1906); van der Waals and Kohnstamm, Lehrbuch d. Thermodynamik.

[3] loc.cit.

the indications given by Langevin. [1]) For the experimental investigation we may refer to Findlay "Der osmotische Druck" (Dresden 1914).

Remarks.

For the pressure on a semi-permeable membrane in the case of very dilute solutions it is, as we see immaterial whether or no there is interaction between the molecules S and the molecules W. Certain other effects of the osmotic pressure, can, however, only be brought about in consequence of such interaction: e.g. the difference of level that comes about between the solution and the pure water, when they are in tubes open at the top, and are in communication through a semi-permeable membrane. Let us consider the following imaginary case: The "sugar" molecules have no interaction at all with the water molecules. It is clear that there cannot ensue a difference of level — the sugar simply evaporates from the solution. When a glass bell-jar is put over the two communicating tubes, the following state of equilibrium is obtained: two solutions of the same concentration on either side with an equally high level. If the two tubes are placed each under a bell-jar of its own, sugar-vapour is formed over the solution with a pressure of the same value as the osmotic pressure of the solution and no difference of level appears then either.

If the difference in level in question is to make its appearance, none of the three following factors can, indeed, be omitted: first the tendency of the sugar to spread (its kinetic pressure), secondly the cohesion of the water, thirdly the interaction of the molecules S and W, without which it would not be possible for the sugar to lift up the water.

Mathematics. — "*On* Nöther's *theorem*". By Dr. W. van der Woude. (Communicated by Prof. Jan de Vries).

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§ 1. Brill and Nöther's well-known paper on algebraic functions [2]) has as starting-point a theorem [3]) shortly before pronounced by Nöther. Its meaning may principally be indicated as follows:

"*A curve F_3 may be represented by the form*

$$F_3 \equiv AF_1 + BF_2,$$

[1]) loc. cit.

[2]) Math. Annalen, 7 (p. 271.)

[3]) Math. Annalen, 6 (p. 351): "Ueber einen Satz aus der Theorie der algebraischen Funktionen."