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Chemistry. — “*The equilibrium solid-liquid-gas in binary systems which present mixed crystals*”. (Third communication). By Prof. H. R. KRUYT and Dr. W. D. HELDERMAN. (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of June 24, 1916).

In two previous communications one of us¹⁾ has discussed the three-phase equilibrium solid-liquid-gas for a binary system when a complete miscibility is possible in all phases; in connexion therewith the system *p*-dichlorobenzene — *p* dibromobenzene has then been investigated. These investigations led to the result that the three-phase line in such a system has usually a different course from that drawn previously²⁾. The general shape proved to be such that on that line a maximum pressure occurs. In Fig. 1 has been drawn

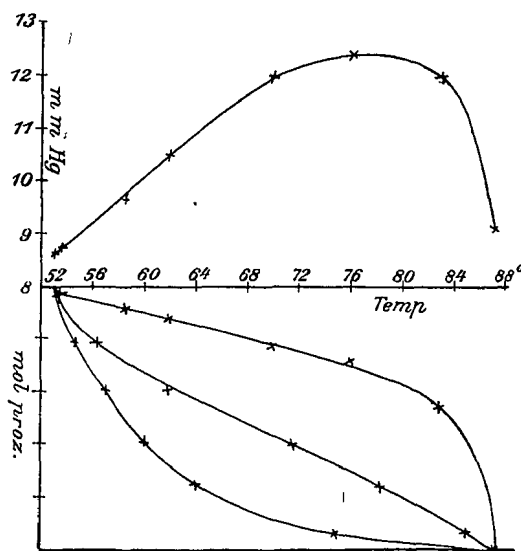


Fig. 1.

a combined PT and Tx projection for the just mentioned system whereas in Fig. 2 the spacial figure is indicated on P, T, x coordinates for this type.

It will be superfluous to describe this figure in detail. Its meaning is plain to any one familiar with the normal figure from BAKHUIS ROOZEBOOM's *Heterogene Gleichgewichte*³⁾.

It is distinguished from the figure mentioned above⁴⁾ by the

¹⁾ H. R. KRUYT, Proc. ^{12, 537-545} ~~18, 542~~ (1909) and ^{13, 206-210} ~~19, 32~~ (1910).

²⁾ H. W. BAKHUIS ROOZEBOOM, Archives Neerlandaises [2] 5, 360 (1900).

³⁾ 2^e Heft pg. 105 (Braunschweig 1904).

⁴⁾ loc cit. previous pg note 2. The figure is also reproduced by H. R. KRUYT, Zeitschr. f. physik. Chem. 79, 657 (1912), Fig. 1.

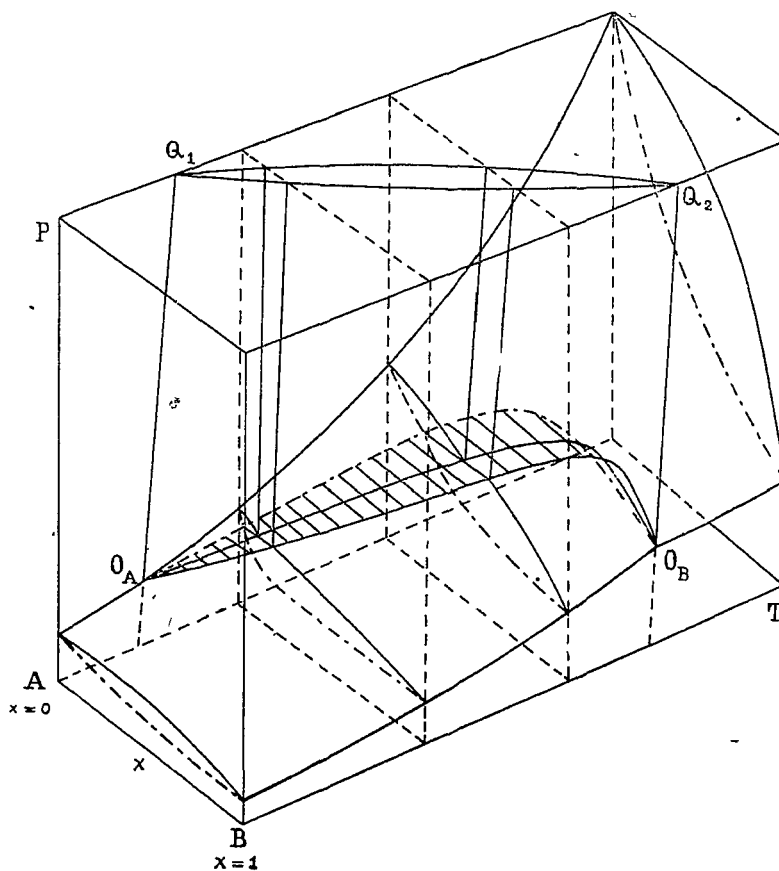


Fig. 2.

peculiarly inflected form of the three-phase region. This has been rendered easily recognisable in Fig. 2 by the additional lines that connect the coexisting phases at each temperature. For further elucidation the lines indicating vapour compositions are shown by --- lines, Px sections are drawn at some temperatures and the Tx melting line has been placed in the upper plane of the figure for the pressure applying to that plane.

2. The result of the previous investigation showing that this figure really represents the normal figure for a system with a continuous series of mixed crystal without a minimum or maximum, makes us expect a peculiar configuration for the system Bromine-Iodine¹⁾ wherein probably a compound IBr occurs; this compound must, however, be credited with the property of being continuously miscible in the solid phase with its products of dissociation, the

¹⁾ P. C. E. MEERUM TERVOGT, Dissertation Amsterdam 1904, Zetschr. f. anorg. Chem., **47**, 203 (1905).

Br and the I. For the melting diagram has a form which is twice that of a system as discussed in the preceding paragraph (see the lower half of Fig. 4) so that both the combinations Br—IBr and IBr—I are comparable therewith. We may thus expect that this system is described by a spacial figure which is a doubling of our Fig. 2.

Here, however, it must be borne in mind that the doubling is not a perfect one because the mixture of 50 atom percent Br and 50 I does not melt sharply, but has a melting range of 1° ; in the melting diagram only narrowing takes place at about the concentration $x = 0.50$. The same applies to the equilibrium L—G. Hence, as no discontinuity occurs at that concentration the two semispacial figures will pass continuously into each other.

Each of the semidiagrams will have to exhibit, in regard to the three-phase tension GLS, a maximum; between those two maxima a minimum must, therefore, be expected.

3. An experimental investigation as to the three-phase pressure GLS in the system Br—I has been started by one of us some years ago; owing to particular circumstances it was postponed but has now been resumed in a somewhat different manner.¹⁾

The purification of the materials used took place in the same manner as with MEERUM TERWOGT. Pure Bromine from KAHLBAUM was first shaken for a few hours with water and then a KBr solution and ZnO were added. This mixture was distilled, the bromine layer distilled again and collected over P_2O_5 . After remaining over night it was distilled off, it passed over entirely at $58^\circ.3$ (corrected) at 751.6 m.m. pressure; nevertheless the first and the last portions of the distillate were not used. The thus made preparation had a sharp melting point at $-7^\circ.4$. The purification of the Iodine took place by subliming *Iodium resublimatum* with addition of KI and then drying over H_2SO_4 .

The *modus operandi* is represented in Fig. 3. In flask A' was contained the mixture of Br and J. BC is a tensimeter containing strong sulphuric acid. The further arrangement E to M serves to compensate the vapour tension of the halogens as much as possible

¹⁾ The investigation in 1912 took place with JACKSON'S glass manometer. There has only been made one preliminary measurement with the mixture of the composition 1Br at $40^\circ.6$. A three-phase pressure of 47.6 mm. of mercury was found. Now a pressure of 48.2 mm. has been found in two independent determinations at $40^\circ.4$. As the three phase tension between 40.4° and 40.6° is indeed falling (see 4 and fig. 4) the agreement is very satisfactory.

with pressure of admitted air so that the sulphuric acid manometer shows but a slight difference in pressure. The compensation pressure is read off on the closed mercury manometer L which is furnished with a plate glass scale thus rendering possible a reading to 0.1 m.m. E is a long india-rubber tube rendering it possible to place the tensimeter in a vertical position inside or outside the thermostat T.

An experiment was carried out as follows: Through the at first open tube D measured portions of Br and I were successively introduced with a long funnel into A; the quantities introduced were determined by weighing the tensimeter. A capillary tube was then sealed to D, and the little flask A was heated until the mixture was wholly fused or nearly so. Then the bulb of the thermometer was slowly cooled to -79° (in the Dewar glass N) and the tensimeter placed horizontally thus causing the sulphuric acid to run into the bulbs C. Halogen vapour was drawn out with a water air-pump and then the capillary tube D connected with P. Q is a long lime tube for the protection of the oil-pump R. The whole apparatus was now carefully evacuated, the capillary was fused off at D and the tensimeter, after a gradual warming, introduced into the thermostat T. In the mean time so much air was admitted into the right half of the apparatus that the sulphuric acid manometer showed but a slight difference in pressure. This was done by means of a three-way cock G. In the tube H was contained air which can be replenished by opening the pinchcock K; a considerable narrowing at I facilitated the regulating. Moreover some modifications in the compensation pressure could be introduced by the displacement of mercury in the gasburettes combination MM. The whole apparatus reminds somewhat of the one employed by MEERUM TERWOGT¹⁾. The measurement of the pressure is here, however, capable of greater accuracy, the pressure compensation is easier whilst the complication near A (a loosely placed in vessel for the reaction mixture) has been omitted as it proved to be superfluous; not once has a tensimeter been broken there.

Reading off the sulphuric acid tensimeter was possible through the pane of glass O of the thermostat.

The density of the acid employed was determined with the sp. gr. bottle at one temperature only; at the other temperatures the table of DOMKE²⁾ was consulted. The thermostat was furnished with a toluene-regulator, a normal thermometer divided to $0^{\circ}.1$ (read off with a magnifying glass) and a constant level arrangement. We

¹⁾ Diss. pag. 37; l. c. pag. 221.

²⁾ Z. f. anorg. Chem. **53**, 125 (1905).

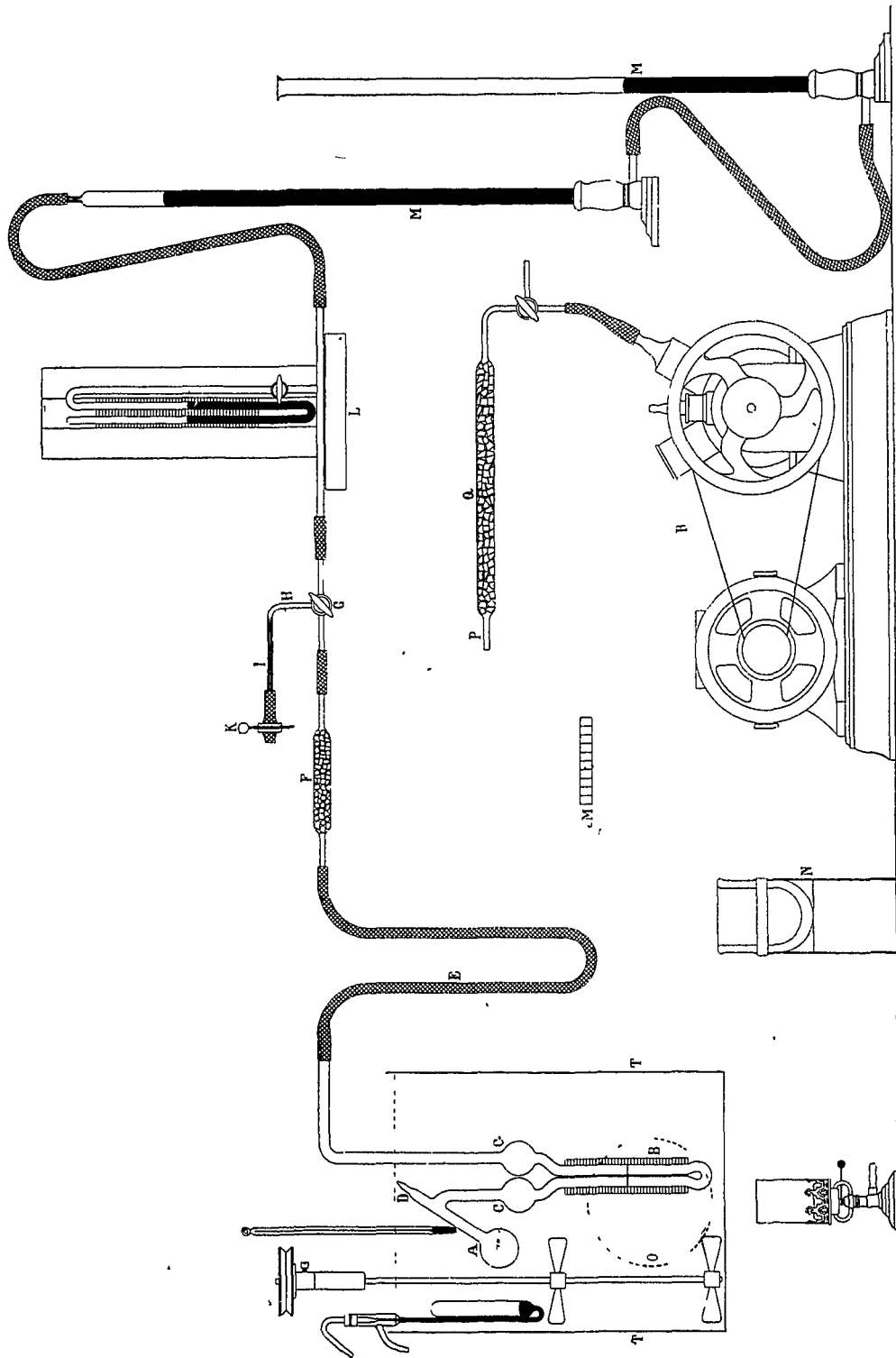


Fig. 3.

chose the experimental temperature in such a manner that we could expect according to TERWOGT'S diagram a partly fused mixture but always satisfied ourselves that this condition in A really existed, which is possible when the apparatus topples over. The experiments were all continued until a perfectly constant end value was attained (usually 24 hours).

4. In the subjoined table are mentioned the results of the experiments. In Fig. 4 they are found indicated graphically combined with the well-known Tx-diagram. The additional triple point tensions are taken from the research of RAMSAY and YOUNG.¹⁾

TABLE.
Three-phase tension in the system Br—I.

Experim. number	Gram Bromine	Gram Iodine	Atom % Iodine	Experiment temperature	Vapour tension in m.m. mercury
11	18.95	14.49	32.5	19.0	83.0
10	16.20	14.49	35.9	23.0	85.8
9	16.20	14.49	35.9	25.0	85.0
2	16.15	19.79	43.6	31.0	79.5
6	15.88	22.52	47.1	36.0	64.1
4	16.25	25.90	50.1	40.4	48.2
1	15.33	24.94	50.5	40.4	48.2
5	15.61	26.11	51.4	42.0	45.4
3	15.55	29.82	54.7	44.3	42.7
7	9.88	23.95	60.4	47.9	54.6
8	9.88	23.95	60.4	50.0	56.7
12	0.93	19.90	92.9	100	> 200

Experiment 12 was executed in the thermostat with boiling water. The three-phase tension was so high that it surpassed the measuring capacity of the manometer.

The results are quite in harmony with the expectations developed in § 2. A plain maximum at 23° and a sharp maximum at 44° have been determined whilst experiment 12 proves the existence of a second maximum.

¹⁾ Journ. chem. Soc. 49, 453 (1886). According to a research of STELZNER and NIEDERSCHULTE Verh. phys. Ges. 7, 159 (1905), the triple point of I would appear to lie a few m.m. higher.

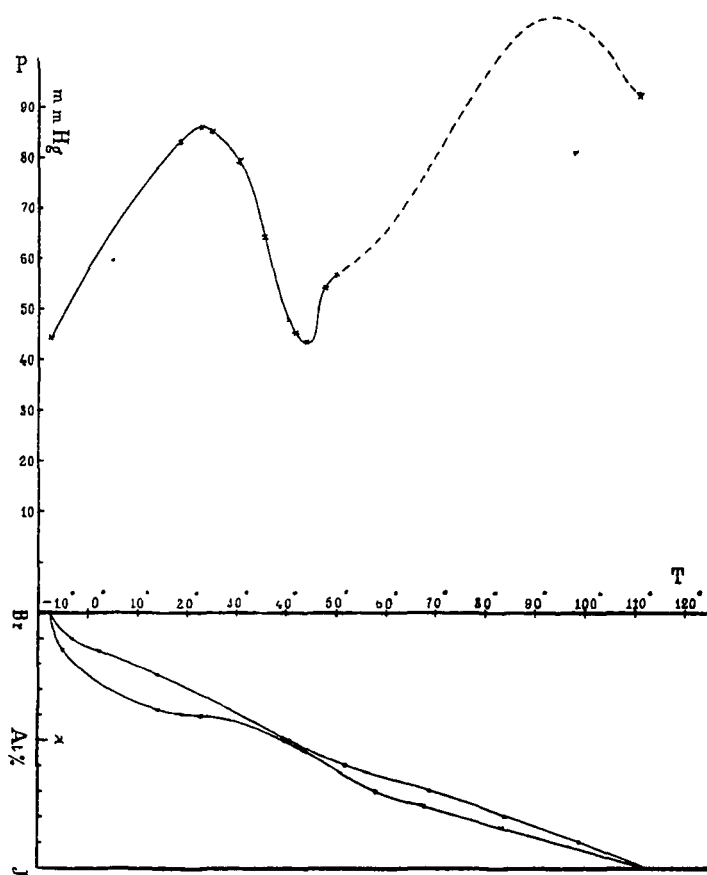


Fig.-4.

We notice that the minimum does not quite lie at the melting temperature of the compound IBr but is removed about 4° to the side of the component with the lower vapour tension.

5. We have sketched in Fig. 5 the spacial figure of a system of the type discussed in this paper. The figures 4 and 5 thus express characteristically that the formation of the compound IBr causes two maxima and an intermediate minimum on the three-phase line whereas in default of that compound only one maximum would occur (Fig. 2). Hence, in the form of the three-phase line we possess a new means of finding a compound in a series of mixed crystals. For we must think that a narrowing in the melting line can only be stated when the interval between liquid and solid branches is large enough to be determined experimentally with sufficient accuracy. This new criterion is all the more welcome because another means cannot be applied to this kind of system. We mean the determination

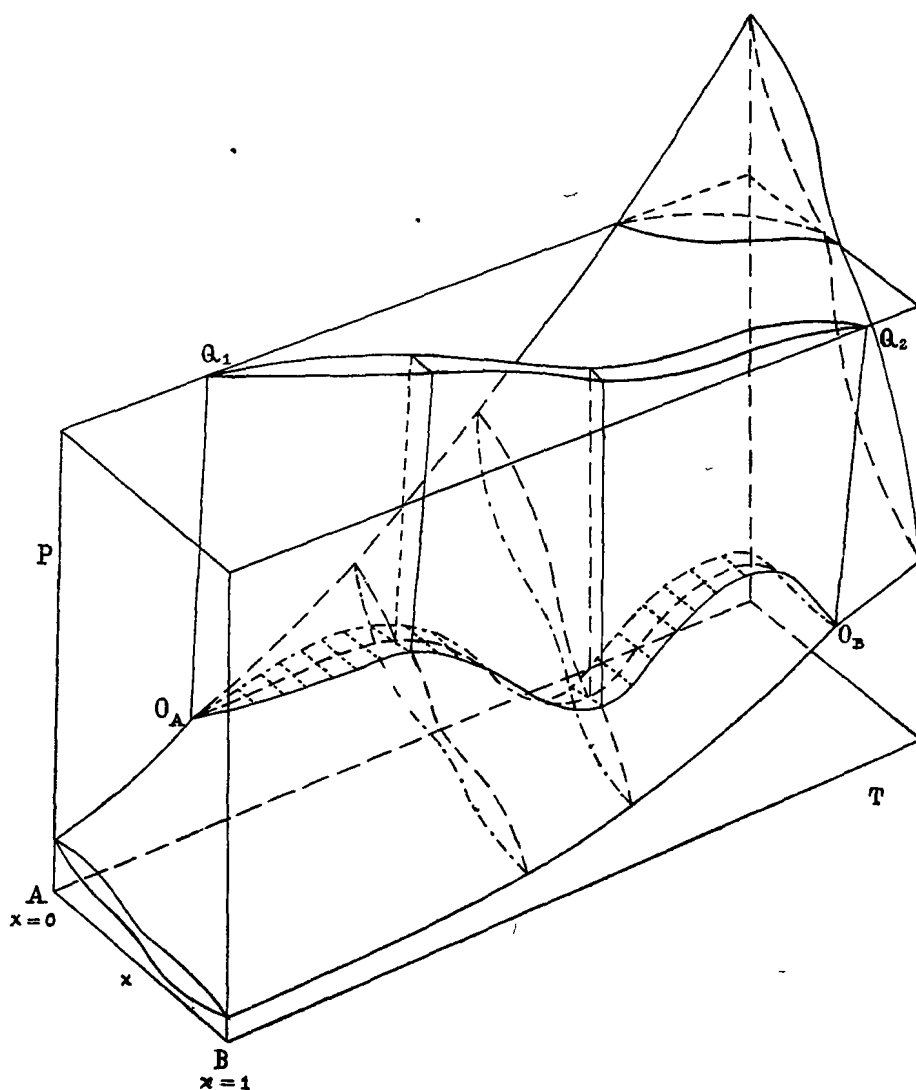


Fig. 5.

of the electric conductivity power, the temperature coefficient thereof, the flow-pressure, the hardness etc., a method which, for instance, has led to such excellent results in the system Mg-Cd¹⁾; in that system the criterion of the three-phase tension is again unsuitable owing to the small value of vapour tension in that system.

The investigation of the three-phase tension in mixed crystal systems can therefore open new points of view in systems where up to the present one has concluded to the absence of compounds and may perhaps lead in other cases to a decision. One might think here of the difference, in the case of optical antipodes, between pseudo-

¹⁾ Compare URASOFF. Z. f. anorg. Chem. **73**, 31 (1912).

racemic mixed crystals and racemic compounds. If, for instance, in the system of *d* and *l*-carvoxim the three-phase tension is to be determined, one might think, in connection with the above that we can perhaps come to a conclusion as to the much discussed question whether we are dealing here merely with a maximum in a series of mixed crystal or whether we are dealing with a racemic compound giving continuous mixed crystal series with the antipodes. Meanwhile it is shown on closer investigation that the resolving of the problem cannot be expected in that manner.

6. The peculiar form of the three-phase line and the correlated spacial figure give rise to different theoretical considerations. We hope to soon revert to the matter, also in connexion with the discussion in the previous paragraph.

Utrecht, June 1916.

VAN 'T HOFF-Laboratory.

Physics — “*The field of n moving centres in EINSTEIN'S theory of gravitation*”. By J. DROSTE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 24, 1916).

1. If in one or other field of gravitation there is placed a particle, i.e. a body so small that, though influenced by the field, it does not itself exercise any influence on the field, it will move in such a way that the first variation of the time integral of

$$L = \left(\sum_{i,j} g_{ij} \dot{x}_i \dot{x}_j \right)^{\frac{1}{2}}$$

calculated after some definite way, is zero. Here $x_4 = t$, and so $\dot{x}_4 = 1$. If $\dot{x}_1, \dot{x}_2, \dot{x}_3$ are small with respect to unity (i.e. nearly the velocity of light), g_{44} will be much larger than say $g_{11}\dot{x}_1^2$. We will call a term one of the first order if, after division by the square of a component of a velocity, it gets a moderate value. Now, as in NEWTON'S theory, which accounts for the phenomena very closely, it follows from the equation of energy that a term, multiplied by the constant of gravity κ , is of the same order as the square of a velocity, we will call also such a term one of the first order and consequently a term, which contains κ^2 , of the second order.

Our purpose is the calculation of L up to the terms of the second order inclusive. If there is no body whatever that can produce a field, we shall have