Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

The considerations, constructions and figures given seem therefore suited to illustrate this part of the theory of VAN DER WAALS. $\dfrac{\mu}{RT}$ is in the case of carbon dioxide and methylchloride a curve slightly bent downwards. Fig. 5 shows how the liquid branch of the binodal line (the rim curve of the liquid part) $\dfrac{\psi}{RT}$ (comp. also the other figures) follows from the curve $\dfrac{\mu}{RT}$ and the curve φ_{ax}.

As to the calculation of $\varphi_{\beta t}$ it should be remarked that $\mathfrak{p}_{max}$ as function of t is known through the vapour tension law, and hence also from the empirical equation of state $\mathfrak{v}_{vcp}$, and that

$$\int_{\mathfrak{v}_{liq}}^{n} \mathfrak{p}\,d\mathfrak{v} = \int_{\mathfrak{v}_{vap}}^{n} \mathfrak{p}\,d\mathfrak{v} + \mathfrak{p}_{max}\,(\mathfrak{v}_{vap} - \mathfrak{v}_{liq}).$$ Especially if $\mathfrak{v}_{liq}$ is small and

hence $\mathfrak{v}_{vap}$ large, (so that at the utmost $\dfrac{B}{v}$ comes into consideration for the deviation from the ideal gas laws) this, when at the same time neglecting $\mathfrak{v}_{liq}$, leads to an important shortening of the calculations.

Neglecting entirely the deviation of the vapour phases from the ideal gaseous state and accepting for a simple substance $log\ \mathfrak{p}_{max} = -f\dfrac{1-t}{t}$ we return to the developments given by VAN DER WAALS in his theory of the ternary mixtures [1]) in which theory many problems about the binary mixtures are developed more in detail.

Physics. — *"The determination of the conditions of coexistence of vapour and liquid phases of mixtures of gases at low tempe- ratures."* By Dr. H. KAMERLINGH ONNES and Dr. C. ZAKRZEWSKI. Communication N°. 92 from the Physical Laboratory of Leiden by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of June 25, 1904).

§ 1. *Introduction.* The two methods for the determination of the molecular coexistence compositions x_l and x_v of the liquid and vapour phases of substances which are gaseous in normal conditions, it is known, can be described as follows. Following the first method we separate small quantities from the two phases at a series of coexistence

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[1]) Proceedings, May 31, 1902, p. 1, sqq.

pressures p and determine each time the composition of those two quantities either by chemical or by physical means.
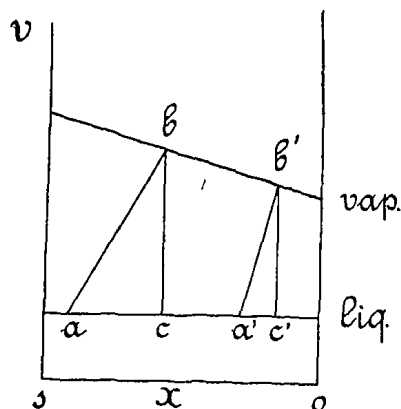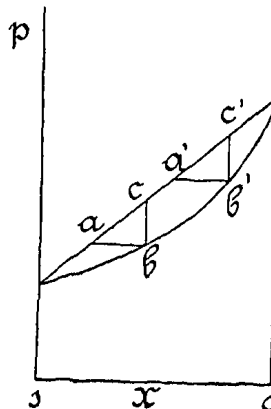

Fig. 1.

Fig. 2.

On the $v\,x$-projection of the binodal curve of the transverse plait on VAN DER WAALS' ψxv-surface for a given temperature T, fig. 1, and also on the $p\,x$ diagram of that binodal line, fig. 2, two such phases are indicated by a and b, for instance. The determination of several pairs of values $a\,b$, $a'\,b'$ etc. gives then the whole course of p, x and v over the transverse plait for T.

If we follow the second method we observe in a series of mixtures with a known composition x, the beginning- and endcondensation phase and determine for them p and v, hence $p_{bx}T$ and $p_{cx}T$, and $v_{bx}T$, and $v_{cx}T$. This investigation comprises each time the phases represented in fig. 1 and 2 by b and c. By combining the results $b\,c$, $b'\,c'$ etc. we can derive again the binodal line and hence the values for x_{lpT}, x_{vpT}, v_{lpT} and v_{vpT}. The application of this last method to low temperatures especially under moderate pressures, forms the subject of this paper.

It is possible to follow also the first method in the case of low temperatures as it has been applied by HARTMAN in Comm. N°. 43 (June '98) for ordinary temperatures. Yet as a rule the analysis of a gaseous mixture is much more difficult than the preparation of a mixture of a definite composition (among others, by means of the mixing apparatus of Comm. N°. 84, Dec. '02) and it is difficult to obtain certainty whether the quantities of vapour and liquid run off have the same composition as the phases which are brought to equilibrium by stirring.

Therefore it is important to solve the difficulty which accompanies

the second method for temperatures below —43° (melting-point of mercury). When we made a first trial in this direction, a high degree of accuracy was not aimed at. In order to answer several questions the accuracy we have reached is sufficient and for the calculation of corrections for more accurate determinations it is quite sufficient.
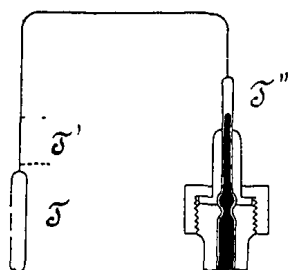
In our measurements we have used the apparatus which is represented schematically in fig. 3. It is in principle a twice bent tube of CAILLETET, of which one end is immersed in the cryostat of the temperature T and filled with a known quantity of a mixture of known composition x, which by forcing up mercury at the ordinary (or higher) temperature T''' is brought to condensation at T.

Fig. 3.

The mixture of which the quantity and the composition x are known, is then only partly contained in the vessel T at the temperature of investigation. Another part is necessarily in a tube at the ordinary or higher temperature T''' which is connected with the vessel by means of a capillary tube. This involves complications, not with regard to the measurement of the begin condensation pressure p_{vx} for the composition x; for until the condensation of the first traces of liquid, with respect to which the vapour is a phase of equilibrium, the composition of the vapour phase in the space at low temperature remains as it was originally, and hence the composition of the vapour phase of equilibrium is perfectly known; but with regard to the determination of the end condensation pressure p_{lx} of the mixture with the composition x. For we cannot condense the whole quantity of the mixture at low temperature. Hence the composition of the liquid phase at T, above which there is a vapour phase of a composition differing in the main from this or the original composition, is no longer indicated by the latter and therefore unknown.

We can, however, find this composition by applying a correction to the original composition x which, as long as the vapour phase occupies only a small volume and remains under a moderate pressure, is not very large (comp. § 5).

§ 2. *General arrangement of the measurements.*

A schematical representation of it will be found on Pl. I, fig. 1. The letters are the same as those used on the plates to which we shall refer.

The volumenometer E (with manometer M, comp. Comm. N°. 84,

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March '03, Pl. II, figs. 1 and 2) contains the gaseous mixture which has been prepared in it by means of the apparatus connected at r_6 and r_8 (comp. Comm. n°. 84). Through the cock r'_9, the steel capillary g_1' and the steel three-way stopcock k (see Comm. N°. 84, Pl. I, fig. 2) it is led to the pressure tube b with calibrated stem (see Comm. N°. 69, April '01, Pl. II) placed in the pressure cylinder $\mathfrak{A}_1'$ (Comm. N°. 84, Pl. I) in order to be compressed by means of mercury from the pressure reservoir C_1' (comp. Comm. N°. 84). Thence through the three-way stopstock k and the steel capillary g_1'' it can be brought under pressure into one of the two apparatus $\mathfrak{D}$ or $\mathfrak{P}$. For the present, according as we wanted to determine either the begin or end condensation pressure p_{bxT} or p_{lxT}, we have connected either the capillary of $\mathfrak{D}$, $\mathfrak{D}_{b_2}$ or that of $\mathfrak{P}$ $\mathfrak{P}_{p_2}$ to the capillary g_1'' by means of sealing wax.

Different from Comm. N°. 84 Pl. I fig. 1 the mercury of the pressure cylinder (see our plate. fig. 1) is also connected by means of n with that of a manometer to determine the pressure in $\mathfrak{D}$ or $\mathfrak{P}$.

By means of the three-way stopcock k the apparatus $\mathfrak{D}$ or $\mathfrak{P}$ may also be connected directly with the volumenometer and then the pressure is measured by means of M.

A detailed representation of the apparatus $\mathfrak{D}$ and $\mathfrak{P}$ is given in figs. 2 and 3 of Pl. I and a description in §§ 4 and 5. In both cases the glass tube to which the mixture which is to be investigated is conducted by means of the capillary g_1'', p in $\mathfrak{P}$ and a in $\mathfrak{D}$, is immersed in a cryostat where the desired temperature is kept in the same way as described in Comm. N°. 83 (Feb. and March '03).

The regulation is brought about for $\mathfrak{P}$ through the exhaust-tube T_{12} and for $\mathfrak{D}$ through the tubes f_4 and m_2. In our measurements we brought liquid methylchloride into the cryostat and the temperature was regulated according to the indications of an alcohol thermometer.

By means of the cock r_8 the volumenometer E is connected not only with the gasreservoirs but also with the mercury airpump so that also the pressure-tube and the test-tube in $\mathfrak{D}$ and $\mathfrak{P}$ can be exhausted. We shall not expatiate on the process of filling the apparatus with a definite quantity of the desired mixture and of measuring any quantity of gas which we allow to escape from them. For the rest we refer to Comm. N°. 84 for the volumenometer and the mixing apparatus, to Comms. N°. 69 and N°. 84 for the pressure cylinder and its appurtenances, to §§ 4 and 5 and Comm. N°. 83 for the cryostats.

§ 3. *Determination of the molecular volume of the coexisting phases.*
As we did not aim at a very high degree of accuracy a few remarks
will be sufficient. As to the liquid phase: with the limitations and
conditions to be treated in § 5, part of the gaseous mixture in the
apparatus $\mathfrak{P}$, called for shortness the piezometer, may by conden-
sation attain a liquid phase of a composition which, as said in § 1,
is derived from x of the original gaseous mixture by a correction.
Measurements with the volumenometer yield the volume that the
liquid phase would occupy in its gaseous state. And by means of the
divisions at p_5 and p_6 Pl. I fig. 3 we read the volume of the liquid
phase itself. The molecular volume of the gaseous phase may best
be derived from the coexistence pressure and from isothermals which
with not too small pressures can be determined after the method
of Comm. N°. 78, April '02, if necessary with the dew-point appa-
ratus $\mathfrak{D}$ itself. With not too large pressure it will in most cases be
possible to apply the correction for the deviation from the law of
BOYLE-GAY-LUSSAC-AVOGADRO by means of the empirical reduced equa-
tion of state (Comm. N°. 71, June '01) according to the law of cor-
responding states.

§ 4. *Beginning of the condensation.* In order to determine this we
have applied the principle of REGNAULT's hygrometer [1]. To this end
we observe the first condensation which is formed in a part of the
apparatus of which the temperature is a little below that of the
surrounding gaseous mixture when the gaseous mixture is brought
to the begin condensation pressure. In order to be able to observe
a very small condensation we have taken for the place of the lowest
temperature a shining mirror, and next to it is placed another mirror
which is not cooled.

The apparatus is blown of one piece in the same way as an ice
calorimeter of BUNSEN. The outer space a has a capacity of about
20 c.c. and is provided with a capillary to which the steel capillary
g'_1, through which the gaseous mixture is led, may be sealed on.
One of the mirrors d is sealed on to the bottom. The inner tube c_2
carries at c_1 the second reflecting surface and serves at the same time
as a cryostat to keep the temperature of this surface constant, a
little below the temperature of the gaseous mixture.

To this end we have devised in the same way as for the outer
cryostat the cover m_1, fitting hermetically on the tube c_5, the small
stirrer h_1 of which the rod h_2 projects through an india-rubber tube

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[1] BATTELLI, (Ann. de Chim. et de Phys. ser. 6, vol. 25, p. 59, 1892), has found
that for pure substances the deposition of liquid on a not cooled mirror placed in
the vapour is a suitable means for the determination of the condensation point.

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as in Comm. N°. 83, and the thermometer i sealed on to m_1 while the vapour of the liquid gas in c_2 is exhausted through m_2.

On the tube c at c_4 the glass cap f_1 is sealed on, through which with an india-rubber stopper the capillary connected to c passes at f_2. This cap forms the cover of the larger cryostat. Through this the apparatus has become very firm and very easy to handle. The capillary b_1 is protected against the stirrer by a metal frame n.

Through the cover at f_3 pass the wires by which the stirrer is suspended. At f_4 the vapour of the bath of liquefied gas is exhausted.

The surfaces of d and c_1 are made reflectors by platinizing them at a redhot temperature with platinum chloride in camomileoil. Though the platinum surface is not so shining as that of a silver mirror, yet the advantages of platinum for this purpose are evident.

The regulation of the temperature in the two cryostats of the apparatus is performed by means of the same exhaust-pump that keeps the pressure constant by means of a pressure regulator (according to the principle of Comm. N° 87, § 3, March '04) in a main tube which branches off into two exhaust-tubes, each shut with a cock.

By adjusting these cocks we can take care that the temperature in the inner cryostat is a little below that of the outer cryostat. What difference of temperature can be kept constant in the two depends on the temperature itself and on the liquid gas.

In measurements to be described in the continuation of this paper the temperature of the large cryostat was — 25°.0 C., that of the small one — 25°.1 C. The required decrease of pressure in the main exhaust-tube could be easily kept up (boiling-point methylchloride — 23° C.) with a water airpump.

The pressure regulator was adjusted at about the pressure belonging to — 25° C. By means of the regulating cocks an assistant took care, as signs were given by another assistant according to the thermometer readings, that both temperatures, hence also the difference between them, remained constant. This could be attained to within 0°.05 C.

The accuracy which we can reach in the determination of the dew-point with our apparatus depends in the first place on the difference of temperature in the two cryostats. As a matter of course it is smaller as the temperature coefficient of the begin condensation pressure is larger. At a given difference of temperature it increases according to the difference of the pressures at which the condensation appears or disappears. The amount of this difference is also determined by the illumination and this is much impaired by the two walls of the cryostat. In our experiments, observations made with the

naked eye with side-illumination of the mirror proved to be the best. The difference ranged between limits which amounted to 2°/₀ of the pressure. The optical part of the method may certainly be much improved. The accuracy attained will, however, be sufficient in many cases.

Adiabatic pressure-variation must naturally be avoided. Yet all such difficulties arise also with measurements at ordinary temperature. With a view to the large dimensions of the vapour space a we have not made use of a stirrer and have tried as much as possible to surmount the difficulties by operating slowly.

§ 5. *Determination of the end condensation pressure.* For this determination the mixture, after the begin condensation pressure is measured, is led back to the volumenometer, the dew-point apparatus is disconnected from the steel capillary and in its place the piezometer p in $\mathfrak{P}$ Pl. I figs. 1 and 3 is connected with the steel capillary g''_1. The piezometer consists of a wide glass tube p_5 Pl. I fig. 3 fastened to a capillary, both graduated and calibrated. The dimensions are chosen with regard to the quantities of gas that may be intended for the measurements. If these are decided upon, the exact quantity of gas, necessary for filling the piezometer at a suitable position of the mercury in the pressure tube b with liquid to near the end of the capillary, must be determined before each determination by means of a preliminary experiment.

The equilibrium of the phases in p_5 is reached by means of a magnetic stirrer q moved by the coil S. The immediate effect of this coil is not sufficient to move the stirrer forcibly through the liquid meniscus. Therefore a soft iron tube z_1 with a groove z_2 which enables us to read on p_6, is moved up and down at the same time with the coil.

This movement ought to be independent from that of the stirrer in the cryostat. But as we did not require a very high degree of accuracy in our experiments we have for simplicity devised the iron tube z as a connection between the upper and the lower part χ_{02} and χ_{04} of the ringshaped valved stirrer (comp. Comm. N°. 83). This is moved up and down mechanically and with the hand in turns, one time to stir the liquid bath, the other time to establish equilibrium between the liquid and the vapour while we simultaneously move the magnetizing coil S.

The essential difference between a determination of the end condensation pressure in our apparatus and that in a CAILLETET tube does not lie so much in the circumstance that we do not liquefy the whole quantity of gas, as in the fact that, as remarked in

§ 1, the temperature is different in the different portions of the gaseous mixture. The portion (see fig. 3 § 1) at the temperature of investigation T is separated from that at ordinary (or higher) temperature T''' by a series of layers (in the capillary) of which the temperatures range from the highest T'' to the lowest T. One of these temperatures we shall call T'.
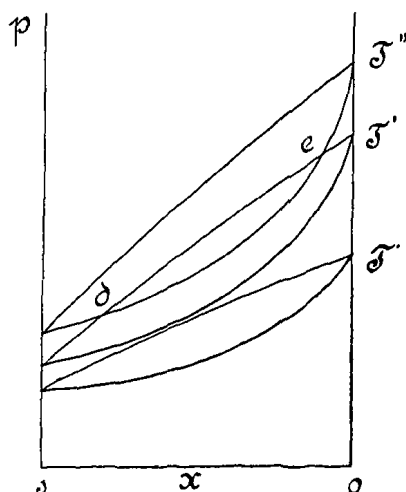

Fig. 4.

This circumstance involves several restrictions and conditions in the application of the method.

In order to make measurements possible for all compositions x the temperature T''' must be taken or raised so high above T, that on the px-diagram (fig. 4) the vapour branch of the binodal curve of T''' does not intersect the liquid binodal curve T. Then we need not fear that condensation begins at T''' while condensation takes place during the transfer 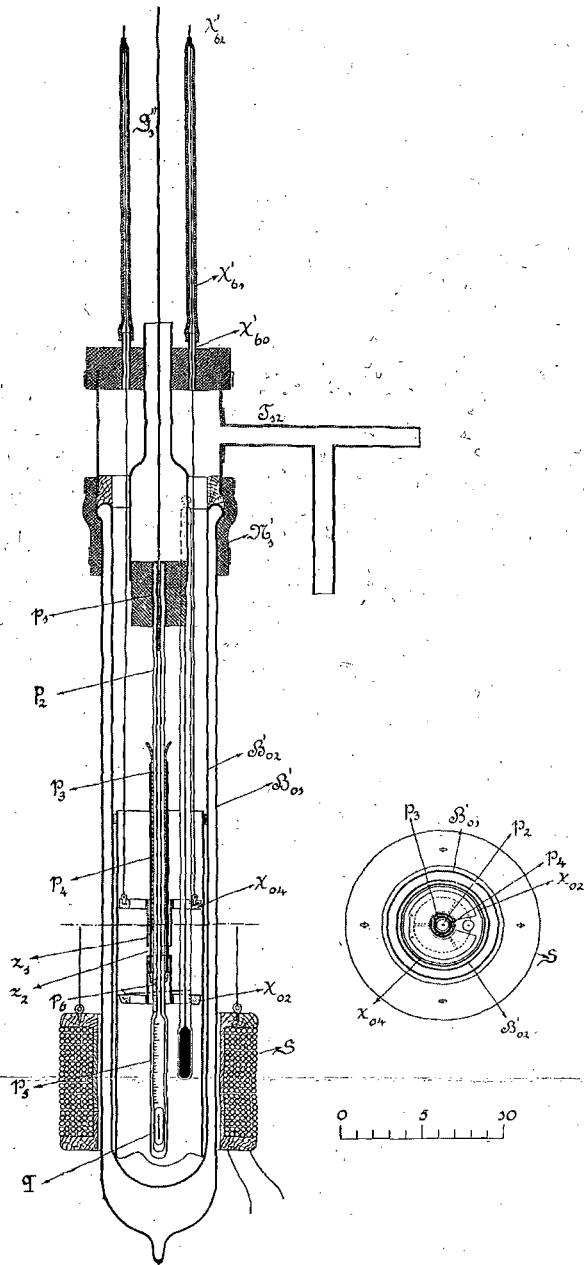of the mixture from the compression tube (or perhaps the volumenometer) to the piezometer. At T'' we then always have a gaseous mixture of the original composition. When the above-mentioned curves intersect, as is represented in fig. 4 for the case of T', we can make measurements only for the compositions represented by points outside the region included approximately between d and e.

Even if, without condensation taking place in the compression apparatus (or perhaps volumenometer) the gaseous mixture can be transferred to the piezometer, the part of the capillary where the temperature falls from T''' to T still offers another difficulty of the same kind. Here we necessarily find temperatures T' at which the vapour branch of the binodal curve of T''' intersects the liquid branch of T'. If drops are formed at T', the composition $x_{l,T}$ of the liquid belonging to the observed coexistence pressure can no longer be indicated. By flowing down and by distillation (the effect of capillarity exceeds that of gravitation) the drops gradually pass over into the liquid phase at T, if care is taken by means of the cock k (see Pl. I fig. 1) and by adjustment of the pressure in b (see Pl. I fig. 1)) that gas streams only into and not out of the piezometer, until finally when we stir with open cock k it appears that equilibrium is reached and the capillary contains vapour only.

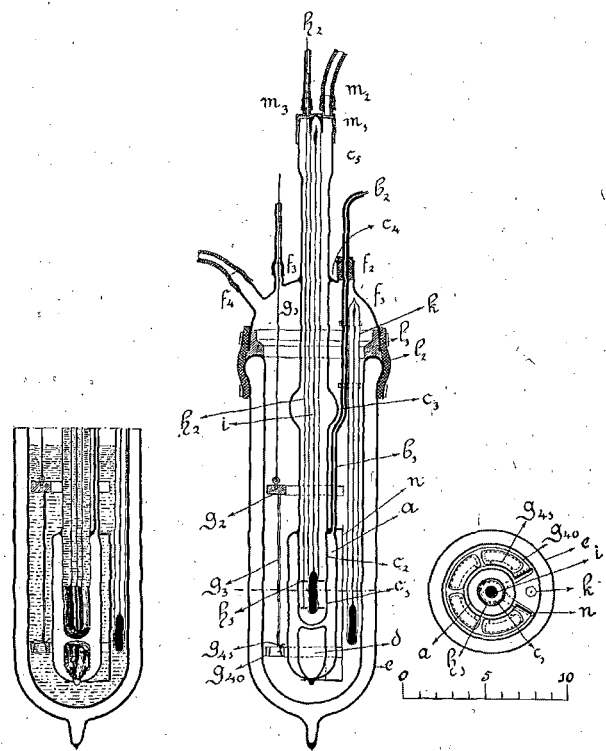, In order to further the distillation and the disappearance of the
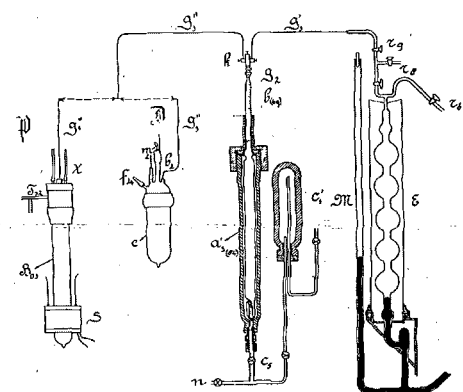
Fig. 3.

Fig. 2.

Fig. 1.

condensation, it is desirable that the capillary at the place where the temperature is between T and T''' should not be too narrow. Moreover the capillary is surrounded by an air jacket p_4, made of a glass tube tightly closed with india-rubber rings p_6 and fish-glue. To avoid diffusion the other portion of the capillary g''_1 must be narrow.

If by previous determinations with the dew-point apparatus we have determined $x_{rp}T$ (as a first approximation it will in some cases be possible to use a preliminary ψ-surface as constructed in Supplement N°. 8 see p. 222), it is easy to apply the correction necessary to derive the composition of the investigated liquidphase at T from x_1, the original composition. On the piezometer divisions the volume of the vapour is read. Let V_v be this volume reduced to normal circumstances and corrected for the first virial coefficient B (comp. for instance the continuation of this paper), let V be the entire volume of vapour and liquid, measured and corrected in the same way, then $V_l = V - V_v$ is the volume of gas, measured and corrected in the same way, which would form the liquid phase.

Hence :

$$X_{lp}T = \frac{X_1\,V - X_{vp}T\,V_v}{V - V_v} = X_1 + \frac{V_v}{V}\,(X_1 - X_{vp}T) + \ldots$$

If we operate under moderate pressures, the correction will be always small and even if $x_{vp}T$ is not very accurately known, it can be applied in a satisfactory way.

Astronomy. — "*A new method of interpolation with compensation applied to the reduction of the corrections and the rates of the standard clock of the Observatory at Leyden,* Hohwü 17, *determined by the observations with the transit circle in* 1903."

By J. Weeder. Communicated by Dr. H. G. van de Sande Bakhuyzen.

§ 4. In the Proceedings of Nov. 29, 1902 occurs a paper "On interpolation based on a supposed condition of minimum," of which the present paper is to be considered as a continuation; this explains the numbering of the sections. In order to interpolate between the ordinates S belonging to the abscissae $t = a, b \ldots y, z$, I have there determined the interpolating curve for which the total sinuosity

$$Is = \int_a^z \left(\frac{d^2 S}{dt^2}\right)^2 dt$$ has the least value. I found that between two suc-