$\dfrac{\Delta p}{\Delta x}$ must rapidly increase. If minimum T_{cr} is exactly on the ether

side, then $\dfrac{1}{a}\dfrac{da}{dx} = \dfrac{1}{b_g}\dfrac{db_g}{dx}$ and so at first the approximate value of

$\dfrac{1}{p}\dfrac{dp}{dx} = -\dfrac{1}{b_g}\dfrac{db_g}{dx}$. But if (rs) differs appreciably from 8, an appreciable

deviation can also occur in this. We find, namely, for p_k not exactly

$\dfrac{1}{27}\dfrac{a}{b_g{}^2}$, but $p_k = \dfrac{1}{27}\dfrac{a}{b_g{}^2}\dfrac{64}{(rs)^2}$ and so $\dfrac{dp_k}{p_k dx} = \dfrac{1}{a}\dfrac{da}{dx} - 2\dfrac{db_g}{b_g dx} - 2\dfrac{d(rs)}{(rs)dx}$. As

the relation $0 = \dfrac{1}{a}\dfrac{da}{dx} - \dfrac{1}{b_g}\dfrac{db_g}{dx} - \dfrac{d(rs)}{(rs)dx}$ holds for minimum T_k, also

$\dfrac{dp_k}{p_k dx} = -\dfrac{1}{b_g}\dfrac{db_g}{dx} - \dfrac{d(rs)}{(rs)dx}$. As, however, at present, both for ether and

for water the observations at T_{cr} are not sufficient to allow us to judge about the variability of b, it must be considered impossible for the present to decide whether (rs) differs for these substances, and if so for which of them (rs) is greater. The value of $\dfrac{dp^r}{p_k dx}$,

which seems greater than $-\dfrac{1}{b_g}\dfrac{db_g}{dx}$ would lead us to expect that (rs)

is smaller for water than for ether. If this variability of b is attributed to the compressibility of the molecule, the water molecule would be more compressible than the ether molecule in spite of its simple structure.

Physics. — "*The calculation of the thermodynamic potential of mixtures, when a combination can take place between the components.*" By J. J. van Laar. (Communicated by Prof. H. A. Lorentz.)

1. In Dr. Hoenen's Thesis for the Doctorate recently published [1] the usual method of calculation also followed by me in the Arch. Teyler [2] and elsewhere is critised on p. 2—4, with which criticism I cannot entirely concur.

In the cited paper in Teyler the problem in question has been treated briefly and not very clearly (in a footnote of a few lines),

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[1] Theorie der thermodynamische functies van mengsels met reageerende componenten en hare toepassingen in de phasenleer; Nijmegen, L. C. G. Malmberg, 1912.

[2] Théorie générale de l'association de molécules semblables et de la combinaison de molécules différentes; Arch. Teyler (2) 11, 3me partie, p. 1—97.

so that what has been said there can easily give rise to misunderstanding.

But for this very reason I have afterwards once more fully discussed the matter in the Chemisch Weekblad [1]). This paper, however, seems to have escaped the notice of the writer of the Thesis.

Fortunately he admits (see p. 4) that a correct formula has been used by me, which leads to *correct results*. I should have been quite satisfied with this, if not some objections called for further elucidation so as to remove any doubt of the validity of the method followed by me in imitation of GIBBS, VAN DER WAALS and others.

2. It is clear that we may *always* write [for convenience'sake we consider again the formation of a compound (association) of the *equal* molecules of an associating substance, which compound is decomposed to an extent β — but the considerations would, of course, apply to *any* compound, also of *unequal* components]:

$$\psi_{v_0,\beta_0} = \psi_{V,\beta} - \int_{v_0,\beta_0}^{V,\beta} \left[\left(\frac{\partial \psi}{\partial v} \right)_\beta + \left(\frac{\partial \psi}{\partial \beta} \right)_v \frac{d\beta}{dv} \right] dv , \quad \ldots \quad (1)$$

because the free energy ψ is a function of both v and β (T taken constant). The quantities v_0 and β_0 refer to an arbitrary condensed gas or liquid state; the quantities V and β to a *very large* gas volume, where accordingly β approaches 1.

Equation 1 is always valid, for the integration is carried out *along the line of equilibrium*, so that the functions ψ then always refer to *states of equilibrium*, but then $\left(\frac{\partial \psi}{\partial \beta} \right)_v$ is always equal to zero in consequence of this equilibrium, and we have simply:

$$\psi_{v_0,\beta_0} = \psi_{V,\beta} - \int_{v_0,\beta_0}^{V,\beta} \left(\frac{\partial \psi}{\partial v} \right)_\beta dv \quad \ldots \quad \ldots \quad \ldots \quad (1^a)$$

In this $\left(\frac{\partial \psi}{\partial v} \right)_\beta = - p$, hence applying VAN DER WAALS's equation of state, we may write: [2])

$$\psi_{v_0,\beta_0} = \psi_{V,\beta} + \int_{v_0,\beta_0}^{V,\beta} \left[\frac{(1+\beta)\,RT}{v-b} - \frac{a}{v^2} \right] dv, \quad \ldots \quad \ldots \quad (1^b)$$

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[1]) Beschouwingen over eenige fundamenteele eigenschappen van den thermodynamischen potentiaal; Chemisch Weekblad 1909, N⁰. 51, p. 1—8.

[2]) For convenience'sake we suppose viz. dissociation of *double* molecules to simple ones, in which $n_1 = -1\beta$, $n_2 = 2\beta$, $\Sigma n_1 = n_1 + n_2 = 1 + \beta$.

in which the quantity β *changes every moment*, namely between the limits of integration β_0 and β, during the integration (see also p. 5 of the paper in the Chemisch Weekblad).

But on account of this variability of β the calculation of (1[b]) is rather laborious, because now also β as a function of v and T is to be substituted, and the integration can then give rise to difficulties.[1])

3. It is therefore of importance to sketch a *second* method of calculation of ψ_{v_0,β_0}, in which the said difficulty is evaded. There is, of course, not the slightest objection to the method discussed just now; against the method that will be given now an objection *may* be raised, though it leads to correct results, as Dr. HOENEN admitted.

We have namely also:

$$\psi_{r_0,\beta_0} = \psi_{V,\beta_0} - \int_{r_0,\beta_0}^{V,\beta_0} \left[\left(\frac{\partial\psi}{\partial v}\right)_\beta + \left(\frac{\partial\psi}{\partial\beta}\right)_c \frac{d\beta}{dv} \right] dv, \quad \ldots \quad (2)$$

in which, therefore, in the case of expansion to a very large volume V *the degree of dissociation β is kept constant*, viz. equal to that of the condensed mixture β_0, which is in internal equilibrium. Now we do not have $\left(\frac{\partial\psi}{\partial\beta}\right)_v = 0$ under the integral sign, for during the expansion the internal equilibrium is disturbed, but $\frac{d\beta}{dv} = 0$, because β remains constant. Just as above we have also here:

$$\psi_{r_0,\beta_0} = \psi_{V,\beta_0} - \int_{r_0,\beta_0}^{V,\beta_0} \left(\frac{\partial\psi}{\partial v}\right)_\beta dv, \quad \ldots \quad (2^a)$$

or also, $\left(\frac{\partial\psi}{\partial v}\right)_\beta$ being again $= -p$, after substitution of the value for p:

$$\psi_{r_0,\beta_0} = \psi_{V,\beta_0} + \int_{v_0,\beta_0}^{V,\beta_0} \left[\frac{(1+\beta_0) RT}{v-b} - \frac{a}{v^2} \right] dv \quad \ldots \quad (2^b)$$

That (1[b]), to which no objections can be raised, and (2[b]) against which an objection *might* be advanced lead to *entirely identical* results, I have demonstrated in the cited paper in the Ch. W. (p. 7—8), which furnishes at the same time an *indirect* proof also of the

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[1]) For also a and b are still functions of β.

validity of (2^b), and it shows that practically the possible objections
to the validity of the second method are unfounded.

4. This objection consists in this that now we do not integrate
along the states of equilibrium, and that it is therefore questionable
whether it is allowed to substitute the known expression of the
mixture β_a as a function of v and T for ψ_{V,β_0}.

Dr. HOENEN says: strictly speaking it is not allowed, but after
some extension of the definitions of the thermodynamic functions, it is.

I will not argue about this, but will only draw attention to what
follows.

In my opinion it is namely not of the least importance in the
calculation of the function ψ for a mixture whether the components
happen to be in equilibrium or not. For what would else be the
meaning of the statement: In case of equilibrium ψ must be a *minimum*!
How can a function be a minimum when the values *outside* the
minimum, where therefore there is no internal equilibrium, are
declared invalid?

Nobody has as yet taken any notice of the said objection, neither
GIBBS in the calculation of the state of dissociation of N_2O_4, nor
VAN DER WAALS[1] in his numerous calculations on these subjects, and
in my opinion justly.

For we write the value of the function ψ for an *arbitrary* mixture
of the components, even though there should be no internal equili-
brium, and *then* determine the *special* values of β for which ψ becomes

minimum, $\left(\text{from } \left(\dfrac{\partial \psi}{\partial \beta}\right)_v = 0\right)$, by which the required concentration
of equilibrium is obtained.

It is namely also possible to regard the mixture fictitiously as
non-reacting (this fiction is realized in many cases of retardation and
similar ones), and write the expression of ψ which the mixture *would*
have if the components really did not interact. For another value of
the ratio of mixing β there is another value of ψ — and for a
definite value of β (independent of the constants of energy and
entropy determining the equilibrium) ψ will have a smallest value.
Then there is really equilibrium, and now no change in the condition
can set in even after ages.

5. Finally I will just reproduce the calculation of § 7 of the cited
paper in the Ch. W. (p. 7—8), in which the identity of the methods,
represented by the formulae (1^b) and (2^b), is proved.

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[1] Cf also VAN DER WAALS-KOHNSTAMM, p. 159 et seq.

Let us introduce the function ζ (the thermodynamic potential) instead of the function ψ (the free energy); then we have to calculate:

$$\zeta_{v_0,\beta_0} = \zeta_{V,\beta} + \int_{v_0,\beta_0}^{V,\beta} \frac{(1+\beta)\,RT}{v}\,dv - p\,(V-v_0) \quad . \quad . \quad . \quad (1^c)$$

and

$$\zeta_{v_0,\beta_0} = \zeta_{V,\beta_0} + \int_{r_0,\beta_0}^{V,\beta_0} \frac{(1+\beta_0)\,RT}{v}\,dv - p\,(V-v_0) \quad : \quad . \quad . \quad (2^c)$$

For the simplicity of the calculation of (1^c), where we have to integrate with variable β, we suppose that also the state v_0, β_0 is a gas-state, to which the simple law of BOYLE applies.

α. Calculation of (1^c). As according to a well-known property :

$$\zeta = n_1 \frac{\partial \zeta}{\partial n_1} + n_2 \frac{\partial \zeta}{\partial n_2},$$

we get :

$$\zeta = (1-\beta)\,\mu_1 + 2\beta\mu_2 = \mu_1 + \beta\,(-\mu_1 + 2\mu_2),$$

with $\dfrac{\partial \zeta}{\partial n_1} = \mu_1$ and $\dfrac{\partial \zeta}{\partial n_2} = \mu_2$ (μ_1 and μ_2 are therefore the *molecular* potentials of the components), and with $n_1 = 1 - \beta$, $n_2 = 2\beta$.

Now on account of the equilibrium (in (1^c) we have namely always states of equilibrium) $-\mu_1 + 2\mu_2 = 0$ [1]), hence simply :

$$\zeta = \mu_1,$$

i.e. the *total* potential of the mixture is equal to the molecular potential of the first (the dissociating) component [or also equal to twice the potential of the second component].

For μ_1 we may now further write at the large gasvolume V:

$$\mu_1 = C_1 - RT\,log\,V + RT + RT\,log\,(1-\beta),$$

in which C_1 is the known temperature function. Hence we may write for (1^c):

$$\zeta_{v_0,\beta_0} = \left[C_1 - RT\,log\,V + RT + RT\,log\,(1-\beta) \right] + RT \int_{v_0,\beta_0}^{V,\beta} \frac{1+\beta}{v}\,dv - p\,(V-v_0).$$

Now for perfect gases (this follows from the condition of equilibrium $-\mu_1 + 2\mu_2 = 0$):

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[1]) For $\dfrac{\partial \zeta}{\partial \beta} = 0$ is identical with $\dfrac{\partial \zeta}{\partial n_1}\dfrac{dn_1}{d\beta} + \dfrac{\partial \zeta}{\partial n_2}\dfrac{dn_2}{d\beta} = 0$, i. e. with $\mu_1\,(-1) + \mu_2\,(2) = 0$, or with $-\mu_1 + 2\mu_2 = 0$.

$$\frac{\beta^2}{1-\beta} = Kv, \quad \ldots \ldots \ldots \ldots \quad (a)$$

hence after logarithmic differentiation:

$$\frac{2-\beta}{\beta(1-\beta)} d\beta = \frac{dv}{v},$$

so that the integral becomes:

$$\int_{r_0,\beta_0}^{V,\beta} \frac{(1+\beta)(2-\beta)}{\beta(1-\beta)} d\beta = \left[\beta + 2\ log\ \frac{\beta}{1-\beta}\right]_{r_0,\beta_0}^{V,\beta} = (\beta-\beta_0) + log\left(\frac{\beta^2}{(1-\beta)^2}\frac{(1-\beta_0)^2}{\beta_0^2}\right).$$

In this according to (a)

$$\frac{\beta^2}{(1-\beta)^2} = \frac{Kv}{1-\beta},$$

hence

$$\int = (\beta-\beta_0) + log\left(\frac{V}{v_0}\frac{1-\beta_0}{1-\beta}\right),$$

and so finally:

$$\zeta_{r_0,\beta_0} = \left[C_1 - RT\ log\ V + RT + RT\ log\ (1-\beta)\right] +$$

$$+ \left[RT(\beta-\beta_0) + RT\ log\ \frac{V}{r_0} + RT\ log\ \frac{1-\beta_0}{1-\beta}\right] - RT(\beta-\beta_0),$$

because $pV = (1+\beta)\ RT$ and $pr_0 = (1+\beta_0)\ RT$.

Hence:

$$\zeta_{r_0,\beta_0} (= (\mu_1)_{r_0,\beta_0}) = C_1 - RT\ log\ v_0 + RT + RT\ log\ (1-\beta_0), \quad (1^d)$$

the known expression for ζ or μ, when also v_0, β_0 refer to a gaseous state.

If the state v_0, β_0 had been a liquid state, the correct expression would have been found too, but in this case the integration would have given rise to great difficulties.

β. Calculation of (2^c). Let us write this equation in the form:

$$\zeta_{r_0,\beta_0} = \zeta_{V,\beta_0} + \int_{r_0,\beta_0}^{V,\beta_0} \frac{\Sigma n_1 \cdot RT}{v} dv - (\Sigma n_1 - (\Sigma n_1)_0)\ RT,$$

then for the molecular potential $\mu_1 = \frac{\partial \zeta}{\partial n_1}$ holds:

$$(\mu_1)_{r_0,\beta_0} = (\mu_1)_{V,\beta_0} + \int_{r_0,\beta_0}^{V,\beta_0} \frac{RT}{v} dv - (1-1)\ RT,$$

because for perfect gases $\dfrac{dv}{v} = \dfrac{\Sigma n_1 . dv_1}{\Sigma n_1 . v_1} = \dfrac{dv_1}{v_1}$ is no longer dependent on the molecular values n_1 etc.

Hence :

$$(\mu_1)_{v_0,\beta_0} = (\mu_1)_{V,\beta_0} + RT \, log \, \frac{V}{v_0},$$

and therefore, if we may again put

$$(\mu_1)_{V,\beta_0} = C_1 - RT \, log \, V + RT + RT \, log \, (1 - \beta_0)$$

for $(\mu_1)_{V,\beta_0}$, also when there is no equilibrium at the degree of association β_0, finally :

$$\zeta_{v_0,\beta_0} = (\mu_1)_{v_0,\beta_0} = C_1 - RT \, log \, v_0 + RT + RT \, log \, (1 - \beta_0), \ldots \quad (2^d)$$

quite identical with (1^d). [For $(\mu_1)_{v_0,\beta_0}$ may namely be written ζ_{v_0,β_0}, because v_0,β_0 represents a state of equilibrium, and hence $\zeta = \mu_1$ (see above)].

This way, which is much shorter than the preceding, and therefore the prevalent one, leads therefore — in spite of $(\mu_1)_{V,\beta_0}$ being changed into its value, if the mixture β_0 is considered as an *arbitrary* one, i. e. apart from the presence or absence of internal equilibrium between the reacting components — to the perfectly accurate expression, which we have found in (1^d) by the much more lengthy but perfectly unobjectionable way.

Baarn, Oct. 21, 1912.

Botany. — *The Linnean method of describing anatomical structures. Some remarks concerning the paper of* Mrs. Dr. MARIE C. STOPES, *entitled : "Petrifactions of the earliest European Angiosperms."* By J. W. MOLL and H. H. JANSSONIUS.

In our "Mikrographie des Holzes der auf Java vorkommenden Baumarten" we are trying to show that important results in systematic Botany can be obtained by anatomical investigations concerning the wood, if these are conducted with sufficient care. For this purpose descriptions of the anatomical structure are necessary, made with careful observance of the rules given by LINNÉ for describing the external appearance of plants. Of course some additions to these rules and some alterations have been necessary, because anatomical and morphological facts belong to somewhat different orders of things and because the microscopic method presents peculiar difficulties. But in the main it is the Linnean method we apply.

The results obtained in the two first volumes of our work are from a systematic point of view most satisfactory, which we hope will become still more apparent, when after some years the work will be finished. Families, genera and in many cases even species