

Citation:

P.E. Verkade, Glutaconic acid. II, in:
KNAW, Proceedings, 18 II, 1916, Amsterdam, 1916, pp. 1527-1539

$$\frac{3}{64} a + \frac{3}{64} (\mu + \mu^{-1}) + \dots \quad (11)$$

This is a straight line which cuts the axis for $a = -(\mu + \mu^{-1})$.

If the difference of temperature which corresponds to this value is found by extrapolating from observations, the quantity ε can thus be deduced. The expansion used in (10) and (11) would nearly always be sufficient in practice. This appears from the following values P of the expression in (9), computed rigorously with $\mu = 1.1$, which is close to the true value for many substances. In the next column the reciprocal value has been inserted; and in the fourth

Extinction P (arbitrary unit).

a	P	$\frac{10}{P}$	$\frac{10 \times}{\text{form. (11)}}$
0	18.58	0.54	1.88
0.05	12.34	0.81	1.93
0.1	10.38	0.96	1.98
1	4.244	2.36	2.82
2	2.871	3.48	3.76
3	2.213	4.52	4.70
7	1.186	8.43	8.45
10	0.885	11.30	11.26
20	0.483	20.72	20.63

column the same quantity, as it would be deduced from the straight line (asymptote of the curve). If necessary one could, of course, also use the rigorous value for comparison with experimental data.

Groningen, February 24, 1916.

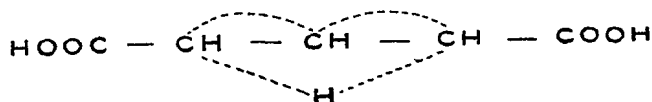
Chemistry. — "*Glutaconic acid*." (II). By Dr. P. E. VERKADE.
(Communicated by Prof. J. BÖESEKEN.)

(Communicated in the meeting of February 28, 1916.)

In the first communication¹⁾ of this series I have shown that in all the known methods of preparing glutaconic acid (and these are very divergent) *exactly the same acid* is obtained; hence this acid is distinguished from possible isomerides by an extraordinary stability.

¹⁾ These Proc. 18. 981 (1915).

As a similar difference in stability has never been noticed in any series of *cis*- and *trans*-isomerides and, in fact, is not to be expected, this result supports to some extent the *normal* configuration of glutaconic acid as figured by THORPE:



If now in glutaconic acid such a floating double bond is really present, this acid (as I already observed in my previous communication) will, as regards its properties, not be absolutely connected either with the genuine *cis*-acids or with the *trans*-acids. We are, however, in a position to predict the following with a fairly high degree of certainty:

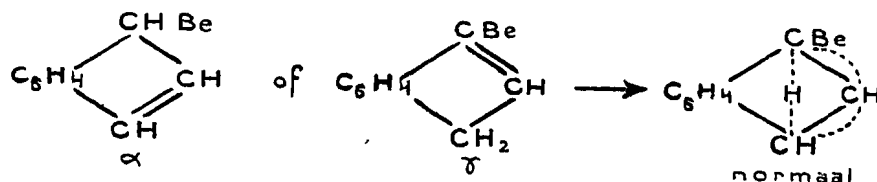
a. as regards its physical properties this acid will occupy a fairly isolated place;

b. when applying the reactions in which a genuine *cis* (respectively, a *trans*) passes into its *trans* (respectively, *cis*) isomeride, no change will take place here as a rule;

c. THORPE has succeeded in obtaining from several of the "normal" alkyl-substituted glutaconic acids, and also from aconitic acid labile modifications (according to THORPE generally real *cis*-, in two cases *trans*-forms).¹⁾ Also in glutaconic acid itself these isomerides will be capable of existing, though they are sure to be exceedingly labile. We may now expect that the ordinary (normal) glutaconic acid, when exposed to some chemical action, is first converted into the *labile modification most favourable for this reaction* and reacts in this labile form.

For the purpose of comparing the properties we, of course, want instances of pure *cis-trans* isomerism. These we possess in the classical isomerism of fumaric and maleic acid, mesaconic and citraconic

¹⁾ COURTOT, for instance, has recently obtained (C. r. 160. 523 (1915)) from the only known *benzylindene* in which, on account of its mode of preparation and properties THIELE (Ann. 347. 249), in my opinion, rightly assumes the presence of a "floating" double bond, a labile isomeride which is reconverted very readily into the well-known ordinary form (for instance, under the influence of alcoholic potassium hydroxide.)



acid etc., but particularly important for our purpose are the three pairs of $\alpha\alpha$ -dialkyl-substituted glutaconic acids ($\alpha\alpha$ -di-Me-, $\alpha\alpha\beta$ - and $\alpha\alpha\gamma$ -tri-Me-acid), which are fully described in the literature; for here is wanting the mobile hydrogen atom of the methylene group and therefore nothing but genuine *cis-trans*-isomerism is possible.

a. *Physical properties.*

1. *Melting point.*

Glutaconic acid melts *completely undecomposed* at 136—138°; not before $\pm 180^\circ$ a slight decomposition sets in. From the situation of the melting point we can deduce nothing, for as shown from the subjoined table, the melting points of the *cis-trans*-isomeric glutaconic acids (contrary to those of the fumaric and maleic acids)

	Cis	Trans
$\alpha\alpha$ -dimethylglutaconic acid	134 – 135°	172°
$\alpha\alpha\beta$ -trimethyl " "	133°	148°
$\alpha\alpha\gamma$ - " " "	125°	150°

differ comparatively but little. On the other hand *cis*- $\alpha\alpha\beta$ - and $\alpha\alpha\gamma$ -trimethylglutaconic acid melt with elimination of water¹⁾, also the mono-alkyl-maleic acids²⁾, whereas the maleic acid itself commences to decompose already a few degrees above its melting point (into anhydride, water and *fumaric acid*).

2. *Solubility.*

As far as solubility in different media is concerned, glutaconic acid behaves almost like its *cis*-homologues. Not altogether so, however, for whereas the latter are, for instance, hardly soluble in concentrated hydrochloric acid (also because a transformation into *trans*-acid may occur here) the glutaconic acid is readily soluble therein; the *cis*- $\alpha\alpha$ and $\alpha\alpha\gamma$ -alkylsubstituted acids are also readily soluble in benzene and chloroform³⁾, which is not the case with glutaconic acid itself.

¹⁾ PERKIN and THORPE: Soc. **71**. 1182 (1897); PERKIN and SMITH: Soc. **85** 155 (1904). As to the $\alpha\alpha$ -acid, nothing is said as to the elimination of water

²⁾ In the solid condition the dialkylmaleic acids are only known in the form of anhydrides.

³⁾ PERKIN and SMITH: Soc. **83**. 8 (1903); **85**. 155 (1904).

3. *Electrical Conductivity.*

The specific conductivity of a glutaconic acid solution of arbitrary concentration (determined directly after dissolving the acid) was, after remaining for three hours at 25°, still *quite unchanged*, even if to the solution had been added a small quantity of hydrochloric acid or aqueous sodium hydroxide. Hence, there was no question of isomerisation in these circumstances.

The dissociation constant of the acid was determined by the method described elsewhere¹⁾. Subjoined are given the results *obtained with acids of different origin*.

A. *At 0°.*

$$\mu_{\infty} = 239.$$

v	ν_v	α	K^0
24.894	15.04	0.0630	1.70×10^{-4}
26.359	20.46	856	1.73
49.788	21.10	882	1.71
92.718	28.52	0.119	1.73
99.576	29.09	122	1.70
199.15	40.18	168	1.70
370.87	53.22	223	1.73
398.30	54.61	229	1.71
741.74	70.46	295	1.72
1483.5	93.31	391	1.70
1593.2	96.14	402	1.70

Mean

$$K^0 = 1.71 \times 10^{-4}.$$

B. *At 25° (see table p. 1531).*

The mean from this and two other series is:

$$K^{25} = 1.76 \times 10^{-4}.$$

WALDEN²⁾ found for an acid of CONRAD m.p. 132°: $K^{25} = 1.83 \times 10^{-4}$ ($\mu_{\infty} = 379.5$); his constants increase somewhat on dilution.

The dissociation constant of glutaric acid is 4.72×10^{-5} ; by

¹⁾ Rec. **35**. 79 (1915).

²⁾ Ph. Ch. **8**. 501 (1891).

the introduction of a double bond (β) into this acid, this constant becomes 3.7 times greater. A same increase is also given by the two alkyl-substituted glutaconic acids which thus far have been

$$\mu_{\infty} = 380.$$

ν	ν_{ν}	α	K^{25}
35.204	28.78	0.076	1.78×10^{-4}
38.638	30.35	798	1.79
70.405	39.81	0.105	1.76
77.276	41.97	111	1.78
140.81	55.01	145	1.75
154.55	58.01	153	1.78
281.62	76.03	200	1.78
309.10	78.95	208	1.76
563.25	102.6	270	1.77
618.20	105.8	279	1.74
704.06	111.6	294	1.75
1126.5	136.0	357	1.76
1236.4	141.2	371	1.77

investigated (and which both contain the mobile H-atom) as is visible from the subjoined table:

	M.p.	K^{25}	Ratio
(labile) β Me-glutaconic acid	116°	1.39×10^{-4}	} $\pm 2.3 : 1$ ¹⁾
(normal) " " "	149°	1.29×10^{-4}	
β Me-glutaric acid	86°	5.9×10^{-5}	
α,β -di-Me-glutaconic acid	146–147°	1.29×10^{-4}	} $\pm 2.3 : 1$ ²⁾
α,γ -di-Me-glutaric acid	140–141°	5.8×10^{-5}	
" " "	127–128°	5.2×10^{-5}	

¹⁾ FICHTER and SCHWAB: Ann. **348**, 251 (1906); ANNA DORN: Dissertation Zürich pag. 19 — WALDEN: Ph. Ch. **8**, 486 (1891).

²⁾ SZYSZKOWSKI: ibid **22**, 172 (1897). On reduction of both α,γ -dimethylglutaconic acids *cis* α,γ -dimethylglutaric acid m.p. 128° is formed exclusively (THORPE and WOOD: Soc. **103**, 276 (1913)).

The very slight difference between the constants of the two β -methylglutaconic acids makes us already suspect that we are not dealing here with an ordinary pair of *cis-trans*-isomerides.

Compared with the unsaturated acids belonging to the succinic series the influence of the double bond is but very slight; for instance, the ratio between mono-alkylfumaric acids and their corresponding alkylsuccinic acids is $\pm 10:1$ and so far as has been ascertained still considerably higher with the maleic acids. In these acids, however, *both* carboxyl groups are attached to the doubly-linked carbon atoms, whereas in the glutaconic acids this is only the case with *one*. This influences no doubt in a considerable degree the dissociation constant.

I deemed it of importance to determine the dissociation constant of this acid also at a still higher temperature; for, *a priori*, the possibility was not excluded that at a higher temperature isomerisation would set in, which would then be recognisable by an abnormal and falling dissociation constant.

The measurements, however, showed that there was no question of isomerisation; the constant was perfectly normal. They were executed at $45^{\circ}.0$ in a conductivity-vessel furnished with a ground glass stopper, so as to prevent the evaporation of the solution. Still the bridge-reading was not yet quite constant. μ_{∞} was determined by interpolation from the values deduced by LUNDÉN¹⁾ for other temperatures.

The results were as follows:

$$\mu_{\infty} = 486.$$

v	μ_v	α	K^{45}
31.379	33.44	0.0685	1.61×10^{-4}
34.691	34.97	720	1.61
62.758	46.40	951	1.59
69.381	48.97	0.101	1.63
125.52	65.00	133	1.63
138.76	67.92	140	1.64
251.03	90.73	186	1.69
277.53	94.11	194	1.68

Mean:

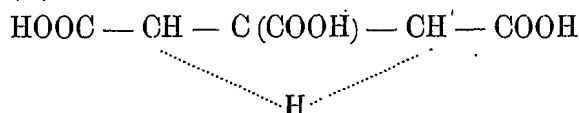
$$K^{45} = 1.64 \times 10^{-4}$$

¹⁾ Samml. chem. und chem.-techn. Vortr. XIV $\frac{1}{3}$ pg. 11. The relation between μ_{∞} and the temperature is fairly well a linear one.

From the dissociation constants found at the different temperatures, it follows that this constant attains in this acid a maximum between 0 and 45°. ¹⁾

4. Heat of combustion.

Neither from glutaconic acid itself, nor from one of its homologues the heat of combustion is already known. We possess, however, trustworthy comparison material for *aconitic acid* (m.p. 191° with decomposition) ²⁾



and tricarballic acid. We find in the literature: ³⁾

for tricarballic acid:	$V_m = 517.0$	resp.	517.3	Kal.
for aconitic acid:	476.5	„	481.5	„
	40.5	„	35.8	„

The mean of these values found by STOHMANN and his co-workers and by LOUGUININE, respectively (and of which the first, for various reasons, is very probably the most trustworthy one) is ± 38 Cal. The usual difference in energy between a saturated aliphatic acid and the correlated unsaturated (*trans*) acid is about 37 Cal. ⁴⁾, whereas, according to investigations of ROTH and WALLASCH ⁵⁾, the heat of combustion of the *cis*-acid is always about 6 Cal. greater than that of the *trans*-acid.

The heat of combustion of "normal" aconitic acid is, therefore, about equal (probably it will be somewhat smaller) to that, which starting from tricarballic acid, we calculate for the *trans*-acid.

From the above we notice that *glutaconic acid* is connected very closely but not completely with the *trans*-acids. It thus stands nearest to the most stable of the two "labile" isomerides which, theoretically, was, of course, to be expected.

b) Mutual transformations of *cis-trans-isomerides*.

BUCHNER ⁶⁾, starting from the ordinary glutaconic acid, has tried

¹⁾ For the position of these maxima see JONES and WHITE: Amer. chem. Journ. 44, and further.

²⁾ Of this acid is still known a "labile" modification m.p. 173° (BLAND and THORPE: Soc. 101, 1490 (1912)).

³⁾ For these heats of combustion compare table 198 of LANDOLT-BÖRNSTEIN-ROTH.

⁴⁾ WALLASCH (Dissertation Greifswald 1913) accepted 45 cal; this value, however, is surely too high.

⁵⁾ Ber. 46 260 (1913).

⁶⁾ Ber. 27. 881 (1894).

to prepare an isomeride thereof: 1st by repeatedly evaporating the acid with concentrated hydrochloric or hydrobromic acid; 2nd by fusion with potassium hydroxide. Both methods, however, gave *negative results*; as could readily be expected there were formed, β -halogenglutaric acids, malonic and acetic acid, respectively.

This also follows from my first communication; it made no difference whether the compound started with was saponified with baryta, aqueous caustic potash or with hydrochloric acid.¹⁾

In the literature we find a number of communications concerning the conversion of the maleic acids into the more stable fumaric acids by treatment with purely chemical agents.²⁾ So far as I am able to judge, *the application of these methods does not cause any change in the glutaconic acid*; hence, there is no sense in further discussing these methods here.

CIAMICIAN and SILBER³⁾ could isolate from solid maleic acid that had been illuminated for 12 months, 12.5% of fumaric acid. This transformation also took place in aqueous solution; according to WISLIGENUS⁴⁾ this reaction can be considerably accelerated by addition of a trace of bromine.

The homologues of maleic acid are, according to the researches of FITTIG⁵⁾ and others, converted exceedingly readily and rapidly into the correlated alkylfumaric acid, by illumination in an ether-chloroform solution after addition of a little bromine.

Conversely, the stable isomerides can be converted into the labile (*cis*) modifications by illuminating in different solvents with ultra-violet light.⁶⁾

I now thought it interesting enough to ascertain how glutaconic acid would behave in these photo-experiments. For this the following experiments were carried out⁷⁾:

1. A quantity of glutaconic acid was spread in a very thin layer on white glazed paper and, after covering with a glass plate illuminated for some months. Each month the melting point of a few specimens was taken; after six months this was still totally unchanged.

2. 1.5 gram of acid (m.p. 134—136) dissolved in 30 cc. of water was illuminated in a tube of uviol-glass from 14 Sept. 1915 to 17

¹⁾ Also compare GUTHZEIT and BOLAM: J. pr. (2) 54. 372 (1896); 58. 407 (1898).

²⁾ Compare MEYER-JACOBSON I 2 p. 417—418

³⁾ Ber. 36. 4267 (1903).

⁴⁾ Ber. 29. R. 1080 (1896).

⁵⁾ Ann. 304. 119. 149 (1899).

⁶⁾ STOERMER. Ber. 42. 4870 (1909).

⁷⁾ I have again to heartily thank Dr. W. D. COHEN for the assistance given during the execution of the two last experiments.

February 1916. The acid then extracted from the solution with ether still had — without any purification — the same melting point.

The remaining aqueous liquid yielded, after careful evaporation in vacuum, no residue.

3. Glutaconic acid was dissolved in as little dry ether as possible. To this solution was added so much pure chloroform that no crystallisation took place as yet, and a trace of bromine. Also here no change had occurred after 14 days exposure to sunlight.

The two last experiments are still being continued.

4. 1.5 gram of acid, dissolved in 15 cc. of water was illuminated in a quartz testtube for a month in front of the quartz-lamp. The liquid slowly turned red; this coloration persisted even after removal from the vicinity of the quartz-lamp. Elimination of carbon dioxide did not take place during the exposure to light. The acid extracted with ether after the illumination proved on investigation to be unchanged, whilst the aqueous solution did not contain any residue. Hence, no β -oxyglutaric acid had formed.

5. The resistance of a glutaconic acid solution contained in a conductivity-vessel was determined at $34^{\circ}.5$ — $34^{\circ}.52$; this was 967.9Ω . Then the quartz-lamp standing just in front of the glass wall of the thermostat was lighted and during the radiation the resistance of the solution was continually controlled. The results were as follows:

0 : 967.9Ω	after 94' : 971.2Ω
after 41' : 967.9	141' : 971.2
60' : 967.9	160' : 973.6
74' : 969.6	197' : 973.6

The change of the resistance is only $\pm 0.6\%$ and in a direction contrary to what might have been expected; it must, therefore be attributed to external circumstances.

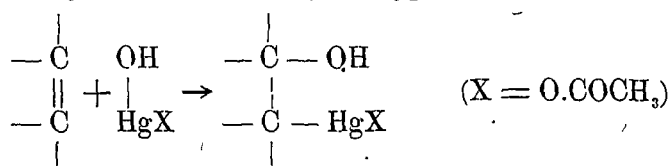
The prediction made in the introduction that glutaconic acid would behave indifferently towards the transformation methods of the *cis-trans*isomeric acids is thus perfectly justified by the facts.

c. Some reactions of glutaconic acid.

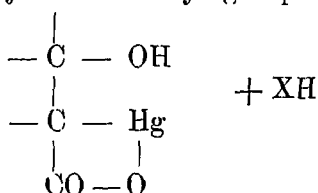
1. BILLMANN¹⁾ has carefully studied the behaviour of a number of unsaturated acids towards mercuric oxide or acetate. He came to the conclusion that of each pair of *cis-trans*isomerides, the stable (*trans*) acid gave a normal mercury salt (for instance cinnamic, fumaric, mesaconic acid) whereas the labile (*cis*) acids caused the

¹⁾ Ber. 35, 2571 (1902); 43, 573 (1910).

formation of compounds wherein carbon-combined mercury occurred (for instance, allocinnamic-, maleic-, citraconic- and itaconic acid). The way the mercury is combined may be typified as follows:



Most of the isolated compounds had, however, a more complicated structure; so for instance the HgX-residue has frequently entered into reaction with an adjacent carboxyl group:



The correctness of these formulae is also shown by the fact that these Hg-compounds, when decomposed with hydrogen sulphide, do not yield the original unsaturated acids, but a β -oxyacid.

The complex salts of the above dibasic acids all contain, however, also normally combined mercury.

It was now suspected that the normal glutaconic acid would react with mercuric acetate *with formation of complex salts* as there exists here the possibility of a transformation into a "labile" *cis*-modification, before the real reaction takes place. This suspicion proved to be correct.

To a warm solution of 5 grams of glutaconic acid in 50 cc. of water a solution of 7.5 grams of mercuric acetate in 300 cc. of water was slowly dropped. After 12 hours the precipitate formed was collected at the pump, washed with water containing some acetic acid, then with alcohol and ether and finally dried in vacuum over phosphorus pentoxide. (Preparation I).

To the warm filtrate 10 grams of Hg-acetate dissolved in 100 cc. of water was once more added. The precipitate formed was now at once collected and treated as before. (Preparation II).

Both specimens are white powders insoluble in water; they dissolve, after a temporary yellow coloration, without any separation of mercuric oxide in dilute alkali and thus *contain exclusively complex-combined mercury*. Just like the compounds obtained by BILLMANN they are soluble with a fairly neutral reaction in potassium chloride and with a faint alkaline reaction in potassium iodide solution.

The mercury determination gave the following results:

Preparation I.

0,1992 grm of substance gave 0,1502 grm HgS : 65,0 % Hg
 0,4329 " " " " 0,3279 " " : 65,3 " "

Preparation II.

0,2885 grm of substance gave 0,2227 grm HgS : 66,5 % Hg
 0,5167 " " " " 0,4000 " " : 66,7 " "

The two preparations are, therefore, probably identical.

Ordinary mercuric glutaconate ought to contain 62.05 % Hg.

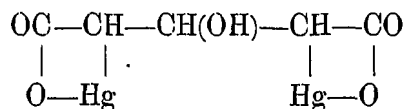
With the ester reaction (strong sulphuric acid + alcohol) it could be shown that no acetyl groups were present in the molecule.

A portion of the substance was dissolved in dilute aqueous sodium hydroxide and the solution saturated with hydrogen sulphide. After addition of a small excess of hydrochloric acid, the precipitated mercuric sulphide was filtered off and the solution (after passing a current of air for some time) concentrated in vacuum. Traces of glutaconic acid were removed by extraction with ether and the aqueous solution was then evaporated to complete dryness. The residual mass was extracted with warm absolute alcohol. After evaporation of this alcohol a brown syrup was left behind which, by the following reactions was identified as β -oxyglutaric acid:

a. a portion of the syrup was heated with a solution of copper acetate and the precipitated Cu-salt, after collecting and washing, decomposed with H_2S . After evaporating the filtrate, I obtained small white needles m.p. 95° .

b. The remainder of the syrup was converted according to the directions of VON PECHMANN and JENISCH¹⁾, into the diphenylhydrazide by means of phenylhydrazine. From glacial acetic acid I obtained this substance in the form of small white crystal-bundles, which on being heated rapidly melt at 236° — 237° , but decompose when heated slowly.

I did not think it of any importance to make a complete analysis of the complex mercuric salt; hence, no definite formula can be given. As, however, the substance contains exclusively complex-combined mercury and as a free COOH-group cannot be assumed because the substance dissolves in dilute potassium chloride solution with a *neutral reaction*, the following formula is about the only possible one:



When crystallising with 3 mols. of H_2O (which is also the water

¹⁾ Ber. 24. 3250 (1891). They give the melting point as 234° — 235° .

content of the citraconic and itaconic acids complexes) the mercury content of this compound is 67.0 %.

Hence, in the molecule of the cis-“labile” glutaconic acid, one of the mobile H-atoms of the methylene group would be substituted by mercury; this can very well be so, for also from the malonic ester and from the malonic acid itself (which also possess a very reactive CH_2 -group) similar simple mercurised derivatives have been prepared by BILLMANN. Moreover, according to the investigations of HENRICH, the H-atoms of the methylene group in the glutaconic ester are replaceable by metals.

2. In the $\alpha\alpha$ -dialkyl-substituted glutaconic acids there exists a great difference between the cis- and trans-forms as regards the velocity of the bromine addition. According to the researches of PERKIN and his co-workers the formation of the corresponding dibromoglutaconic acid proceeded very readily with the cis-acids; when exposed in a thin layer to the action of bromine vapour the absorption was complete in a few hours. On the other hand the trans-acids were either not at all or but very slowly attacked in this method.

If now the “normal” glutaconic acid is exposed to the action of bromine we can expect here *via the cis-labile form* a rapid assimilation of bromine.

This expectation was not doomed to disappointment. Finely powdered glutaconic acid spread out in a very thin layer on a watch-glass and placed in a desiccator at the bottom of which was placed a layer of bromine, had practically absorbed the theoretical quantity of bromine in a few hours.

The powder thus obtained was recrystallised from a little formic acid (D 1.21) or from chloroform.

$\alpha\beta$ -Dibromoglutaric acid forms a white crystalline mass m.p. 152° readily soluble in water and ether, less so in chloroform and very sparingly in petroleum ether or benzene. The titration of the acid gave the following result:

0.3040 gram required	22.23 cc.	0.0947 n. baryta:	$M = 289.2$
0.1954 „ „	14.26 cc.	„ „	289.7
		theory	$M = 290.0$

A bromine determination gave:

0.1632 gram of substance yielded	0.2121 grm. AgBr.	Found : $55.30\% \text{ Br.}$
		theory : $55.15\% \text{ Br.}$

In aqueous solution, glutaconic acid also takes up bromine fairly

rapidly, on the other hand very slowly in glacial acetic acid or chloroform¹⁾; the reaction may, however be accelerated under the influence of daylight.

Maleic acid behaves in quite an analogous manner; the velocity of absorption, however, (as might be expected from the constitution) is *greatest with glutaconic acid*.

From the material communicated in this treatise I believe it may be safely concluded that the symmetric formula of THORPE is indeed a fairly proper interpretation of the properties of glutaconic acid.

In the following communication, I hope to elucidate this formula with a model.

Delft, February 15, 1916.

Chemistry. — “*In-, mono- and divariant equilibria.*” VIII. By
Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of March 25, 1916).

12. *Further consideration of the bivariant regions; the turning lines.*

The different properties of the curves and the regions, which we have deduced in the previous communications, are only true under some conditions, which we have up to now assumed silently. They are valid viz. not only in the immediate vicinity of the invariant point, but still also at some distance, viz. under the conditions:

1. the points under consideration must not be situated in the P, T -diagram too far from the invariant point; consequently the P and T of the equilibria under consideration must not differ too much from the P and T of the invariant point;

2. the compositions of the occurring phases must not differ too much from the compositions, which they have in the invariant point.

Further we shall indicate somewhat more exactly what is the meaning of “not too far” and “not too much” in these conditions.

As long as those conditions are satisfied, the deduced properties remain valid; when they are not satisfied, deviations may occur.

When all phases have a constant composition, the latter condition is always satisfied; this should be the case in fig. 1 (II) for instance when one of the phases represents watervapour and the others

¹⁾ The bromination in chloroform in sun-light is the best way of preparing the $\alpha\beta$ -dibromoglutaric acid. There are always formed, however, small quantities of by products (probably higher brominated ones).