

Individual Activity Coefficients of Ions in Aqueous Solutions

BY JACOB KIELLAND¹

Lewis and Randall² in 1923 published a table of 26 individual ionic activity coefficients, which has subsequently been of frequent use to chemists. The authors emphasized, however, that the presented values should be regarded as preliminary values only. In 1927 Redlich³ reprinted the same table, and no corrections were made even by Jellinek⁴ in his comprehensive textbook of 1930.

It has been pointed out⁵ that the concept of individual activity coefficients cannot be defined accurately, and such coefficients may not even be determined experimentally without some supplementary definition of non-thermodynamic nature. But the concept may not be the less, and has often been, quite useful,^{6,7} when estimating mean ionic activity coefficients in cases where great accuracy is not claimed.

It is the purpose of the present paper to present a revised and extended table of ionic activity coefficients, which has largely been computed by independent means, taking into consideration the diameter of the hydrated ions,⁸ as estimated by various methods.

For sufficiently dilute solutions one may use the well-known Debye-Hückel formula (aqueous solution at 25°)

$$\log f_i = \frac{-0.358 z_i^2 \Gamma^{1/2}}{1 + 10^8 a_i 0.2325 \Gamma^{1/2}} = \log \gamma_i + \log \left(1 + 0.018 \sum_{i=1}^s m_i \right) \quad (1)$$

where f_i denotes the rational,⁹ and γ_i the practical activity coefficient of the i th ion with valence z_i , and Γ is the ionic concentration given by $\sum_{i=1}^s c_i z_i^2$ with c_i in moles per liter.

It has been shown recently by Brüll¹⁰ that a_i

(1) Research chemist, Norsk Hydro-Elektrisk Kvaestofaktieselskab.

(2) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

(3) G. N. Lewis and M. Randall, "Thermodynamik," translated and with supplementary notes by O. Redlich, Verlag von J. Springer, Wien, 1927.

(4) K. Jellinek, "Lehrbuch der physikalischen Chemie," Vol. III, Ferd. Enke, Stuttgart, 1930.

(5) E. A. Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929).

(6) E. A. Guggenheim and T. D. Schindler, *ibid.*, **38**, 533 (1934).

(7) G. Scatchard, *Chem. Rev.*, **19**, 323 (1936).

(8) The part of the effect on $\log f_i$, which is taken into account by the increase of a_i caused by the hydrated water molecules, is rather small in the case of some anions and a few cations, but may be of more importance in other cases—compare diameters of hydrated and not hydrated ions in Table I.

(9) E. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

(10) L. Brüll, *Gazz. chim. ital.*, **64**, 624 (1934).

may be regarded as the effective diameter of the hydrated ion. The individual a_i -values may now be approximately calculated by different methods—for example from the crystal radius and deformability, according to the following equation for cations, given by Bonino¹¹

$$10^8 a_i / z_i = 0.9 \cdot 10^8 r_i / 10^{24} \alpha_i + 2 \quad (2)$$

or from the ionic mobilities, using the well-known equation

$$10^8 a_i = 182 z_i / l_\infty \quad (3)$$

or its empirical modification, given by Brüll¹⁰

$$10^8 a_i = 216 z_i^{1/2} / l_\infty \quad (4)$$

One can also determine the chemical hydration number by the entropy deficiency method of Ulich,¹² and calculate a_i from this and the effective radius of the ion.

Results

The diameters of a number of inorganic and organic ions, hydrated to a quite different extent, have been calculated by these methods, and the results are shown in Table I. Values of "effective" ionic radii (r_i) were taken from Grimm and Wolff,¹³ deformability α_i of ions from Born and Heisenberg¹⁴ or calculated from the ionic refraction R by the equation

$$10^{24} \alpha = 3 \times 10^{24} R / 4\pi N = 0.395R \quad (5)$$

Errera's values for R being introduced.¹⁵ Ionic mobilities and entropies have been taken from Landolt-Börnstein.¹⁶ Entropy and chemical hydration numbers of some gaseous anions were estimated roughly by the author. The parameters of the other anions, and of the organic ones, have been calculated from ionic mobilities only, and are therefore not included in the table (they are, however, to be found in Table II).

When computing the activity coefficients from the Debye-Hückel formula, it was decided to arrange the various ions in groups according to the

(11) G. B. Bonino and G. Centola, *Mem. Accad. Italia*, **4**, 445 (1933).

(12) H. Ulich, *Z. Elektrochem.*, **36**, 497 (1930); also J. Kielland, *J. Chem. Ed.*, in press.

(13) H. G. Grimm and H. Wolff, *Z. physik. Chem.*, **119**, 254 (1926); see also K. Fajans and K. F. Herzfeld, *Z. Physik*, **2**, 309 (1920).

(14) M. Born and W. Heisenberg, *ibid.*, **23**, 388 (1924).

(15) J. Errera, "Polarisation Diélectrique," Presses Universitaires, Paris, 1928, p. 144.

(16) From Landolt-Börnstein *Physikalisch-chemische Tabellen*, 5. Aufl. III Erg. bd., Verlag von Springer, Berlin, 1936, and other sources.

TABLE I

PARAMETER $10^8 a_i$ AS ESTIMATED BY VARIOUS METHODS

Ion	Effective diam. of unhydrated ion (eq. 2)	Bonino formula (eq. 2)	Ionic mobilities (eq. 3) (eq. 4)		Hydration no. and eff. radius	Rounded values (Table II)
Li ⁺	0.8	6.2	4.7	5.6	5.3	6
Na ⁺	1.0	4.2	3.6	4.3	4.7	4-4.5
K ⁺	1.6	2.8	2.5	2.9	3.9	3
Rb ⁺	1.8	2.45	2.4	2.8	...	2.5
Cs ⁺	2.1	2.35	2.35	2.8	...	2.5
NH ⁺	2.45	2.9	...	2.5
Tl ⁺	1.4	2.15	2.4	2.9	...	2.5
Ag ⁺	1.5	2.35	2.95	3.45	4.7	2.5
Be ²⁺	0.6	...	8.1	6.8	...	8
Mg ²⁺	.9	10	6.85	5.8	7.0	8
Ca ²⁺	1.4	6.25	6.1	5.15	6.3	6
Sr ²⁺	1.7	5.1	6.1	5.15	...	5
Ba ²⁺	2.1	4.9	5.7	4.8	5.9	5
Ra ²⁺	2.3	...	5.45	4.55	...	5
Cu ²⁺	6.5	5.45	6.8	6
Zn ²⁺	1.1	6.05	6.8	5.75	6.8	6
Cd ²⁺	1.4	5.0	6.75	5.65	6.4	5
Hg ²⁺	1.5	4.9	6.3	5
Pb ²⁺	...	4.5	5.2	4.35	5.9	4.5
Mn ²⁺	1	5.2	6.8	5.7	...	6
Fe ²⁺	1	...	6.8	5.7	6.8	6
Ni ²⁺	1	5.6	6.8	5.7	...	6
Co ²⁺	1	...	6.8	5.7	...	6
Sn ²⁺	6.2	6
Al ³⁺	0.8	...	8.65	6.0	> 8	9
Fe ³⁺	8.05	5.5	> 8	9
Cr ³⁺	8.15	5.6	...	9
La ³⁺	2.0	7.7	7.8	5.4	...	9
Ce ³⁺	8.15	5.6	...	9
Pr ³⁺	8.35	5.75	...	9
Nd ³⁺	8.5	5.8	...	9
Sc ³⁺	1.4	10.8	8.45	5.8	...	9
Sm ³⁺	8.3	5.7	...	9
Y ³⁺	1.6	8.15	9
In ³⁺	1.4	8.95	9
Sn ⁴⁺	...	12.5	11
Th ⁴⁺	2.2	10.3	11
Zr ⁴⁺	1.6	11.5	11
Ce ⁴⁺	2.0	11	11
F ⁻	1.5	...	3.3	3.9	5.3	3.5
Cl ⁻	1.9	...	2.4	2.85	3.9	3
Br ⁻	2.0	...	2.3	2.75	3.6	3
I ⁻	2.2	...	2.4	2.8	2.9	3
ClO ₃ ⁻	2.85	3.35	3.3	3.5
ClO ₄ ⁻	2.7	3.15	3.5	3.5
NO ₃ ⁻	2.55	3.0	3.1	3
BrO ₃ ⁻	3.25	3.85	3.5	3.5
IO ₃ ⁻	4.45	5.25	4.8	4-4.5
HCO ₃ ⁻	4.1	4.85	7	4-4.5
S ²⁻	2.2	5	5
CO ₃ ²⁻	4.25	5.05	6	4.5
SO ₄ ²⁻	3.8	4.55	5 1/2	4
CrO ₄ ²⁻	4.2	5.0	5 1/2	4.5

parameters found above, and use rounded values of a_i , as clearly stated in Table II, where the resulting activity coefficients are given. (The parameters of hydrogen and hydroxyl were not calculated independently, but taken as 9 and 3.5 Å.)

Approximate Formulas

Guggenheim and Schindler⁶ have proposed the following formula for ionic activity coefficients up to an ionic concentration of about $\Gamma = 0.2$

$$\log f_i = -0.5 z_i^2 \mu^{1/2} / (1 + \mu^{1/2}) \quad (6)$$

$$\text{which equals } -0.354 z_i^2 \Gamma^{1/2} / (1 + 3.04 \times 0.2325 \Gamma^{1/2}) \quad (7)$$

This equation is based on a parameter $a_i = 3$ Å. for all ionic species. Of the about 130 ions examined by the author, 20% have a diameter of 2.5 to 3.5 Å., 40% 4 to 5 Å., 25% 6 to 8 Å., and 15% 9 to 11 Å. The inorganic univalent ions are most frequently of the order 3 to 4 Å., the divalent ones 4 to 6 Å., the trivalent about 9 Å. and the tetravalent about 11 Å., while the organic ions fall between 4.5 to 7 Å. Hence, one may suggest the following formulas, which in the case of univalent ions give the same results as Guggenheim's, but which in the case of organic and polyvalent ions give distinctly higher values for the activity coefficients.

$$\text{Inorganic ions}^{17} \quad \log f_i = -0.5 z_i^2 \mu^{1/2} / (1 + z_i \mu^{1/2}) \quad (8)$$

$$\text{Organic ions} \quad \log f_i = -0.5 z_i^2 \mu^{1/2} / (1 + 2\mu^{1/2}) \quad (9)$$

Such formulas as the following of Guggenheim⁶

$$-\log f_i = 0.5 z_i^2 \mu^{1/2} / (1 + \mu^{1/2}) + \sum_K B_{ik} c_k \quad (10)$$

or that of Brüll¹⁸

$$-\log f_i = 0.358 z_i^2 \Gamma^{1/2} / (1 + 10^8 a_i 0.2325 \Gamma^{1/2}) + A(\Gamma^{1/2} + \Gamma^{3/2}) \quad (11)$$

may be more accurate in the more concentrated range, but they contain additional constants, which must be determined by the activity coefficient measurements themselves.

Comparison with Experimental Values

The individual ionic activity coefficients computed in this paper with independently estimated a_i -values (except in the case of H⁺), have been compared with those obtained experimentally by Hass and Jelinek¹⁹ in the case of Cl⁻, Br⁻, I⁻, SO₄²⁻ and (COO)₂²⁻, and with those found by Bjerrum and Unmack²⁰ in the case of H⁺, PO₄³⁻ and citrate³⁻. In Fig. I we have plotted these values, which agree fairly well with the calculated ones (drawn lines).

(17) Except such complexes as the ferrocyanides, cobaltamines and others which are to be treated as organic ions by the formula 9.

(18) L. Brüll, *Gazz. chim. ital.*, **64**, 261, 270 (1934).

(19) K. Hass and K. Jelinek, *Z. physik. Chem.*, **A162**, 153 (1932). The activity coefficients of SO₄²⁻ were recalculated, using the more recent value 0.614 for the normal potential of the mercurous sulfate electrode [Shrawder, Cowperthwaite and La Mer, *THIS JOURNAL*, **56**, 2348 (1934)] together with the best value 0.222 for that of the silver chloride electrode (ref. 16, p. 1855). When computing the solubility product of silver oxalate, we extrapolated against the function $\mu^{1/2} / (1 + 1.5\mu^{1/2})$ (H. and J. used $\mu^{1/2}$), and found it to be $1.3 \cdot 10^{-11}$ at 25°. Hence, all activity coefficients of oxalate anion (as found by H. and J.), were multiplied by 1.2.

(20) N. Bjerrum and A. Unmack, *Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd.*, **9**, 1 (1929).

TABLE II
INDIVIDUAL ACTIVITY COEFFICIENTS OF IONS IN WATER

Parameter	Total ionic concentration $\Gamma = \sum_{i=1}^s c_i z_i^2$								
	$10^3 a_1$	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
Inorganic ions:									
H ⁺	9	0.975	0.967	0.950	0.933	0.914	0.88	0.86	0.83
Li ⁺	6	.975	.965	.948	.929	.907	.87	.835	.80
Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Tl ⁺ , Ag ⁺	2.5	.975	.964	.945	.924	.898	.85	.80	.75
K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻	3	.975	.964	.945	.925	.899	.85	.805	.755
OH ⁻ , F ⁻ , NCS ⁻ , NCO ⁻ , HS ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻	3.5	.975	.964	.946	.926	.900	.855	.81	.76
Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₄ ⁻ , H ₂ AsO ₄ ⁻ , [Co(NH ₃) ₄ (NO ₂) ₂] ⁺	4-4.5	.975	.964	.947	.928	.902	.86	.82	.775
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₆ ²⁻ , S ₂ O ₈ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻	4	.903	.867	.803	.740	.660	.545	.445	.355
Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻ , [Co(NH ₃) ₅ Cl] ²⁺ , [Fe(CN) ₆ NO] ²⁻	4.5	.903	.868	.805	.742	.665	.55	.455	.37
Sr ²⁺ , Ba ²⁺ , Ra ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₄ ²⁻ , WO ₄ ²⁻	5	.903	.868	.805	.744	.67	.555	.465	.38
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺	6	.905	.870	.809	.749	.675	.57	.485	.405
Mg ²⁺ , Be ²⁺	8	.906	.872	.813	.755	.69	.595	.52	.45
PO ₄ ³⁻ , [Fe(CN) ₆] ³⁻ , [Cr(NH ₃) ₆] ³⁺ , [Co- (NH ₃) ₆] ³⁺ , [Co(NH ₃) ₅ H ₂ O] ³⁺	4	.796	.725	.612	.505	.395	.25	.16	.095
[Co(ethylenediamine)] ³⁺	6	.798	.731	.620	.52	.415	.28	.195	.13
Al ³⁺ , Fe ³⁺ , Cr ³⁺ , Sc ³⁺ , Y ³⁺ , La ³⁺ , In ³⁺ , Ce ³⁺ , Pr ³⁺ , Nd ³⁺ , Sm ³⁺	9	.802	.738	.632	.54	.445	.325	.245	.18
[Fe(CN) ₆] ⁴⁻	5	.668	.57	.425	.31	.20	.10	.048	.021
[Co(S ₂ O ₃ (CN) ₆] ⁴⁻	6	.670	.575	.43	.315	.21	.105	.055	.027
Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺	11	.678	.588	.455	.35	.255	.155	.10	.065
[Co(SO ₃) ₂ (CN) ₄] ⁵⁻	9	.542	.43	.28	.18	.105	.045	.020	.009
Organic ions:									
HCOO ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₃ ⁺ , (CH ₃) ₂ NH ₂ ⁺	3.5	.975	.964	.946	.926	.900	.855	.81	.76
NH ₃ +CH ₂ COOH, (CH ₃) ₃ NH ⁺ , C ₂ H ₅ NH ₃ ⁺	4	.975	.964	.947	.927	.901	.855	.815	.77
CH ₃ COO ⁻ , CH ₂ ClCOO ⁻ , (CH ₃) ₄ N ⁺ , (C ₂ H ₅) ₂ - NH ₂ ⁺ , NH ₂ CH ₂ COO ⁻	4.5	.975	.964	.947	.928	.902	.86	.82	.775
CHCl ₂ COO ⁻ , CCl ₃ COO ⁻ , (C ₂ H ₅) ₃ NH ⁺ , (C ₃ H ₇)NH ₃ ⁺	5	.975	.964	.947	.928	.904	.865	.83	.79
C ₆ H ₅ COO ⁻ , C ₆ H ₄ OHCOO ⁻ , C ₆ H ₄ ClCOO ⁻ , C ₆ H ₅ CH ₂ COO ⁻ , CH ₂ =CHCH ₂ COO ⁻ , (CH ₃) ₂ C-CHCOO ⁻ , (C ₂ H ₅) ₄ N ⁺ , (C ₃ H ₇) ₂ - NH ₂ ⁺	6	.975	.965	.948	.929	.907	.87	.835	.80
[OC ₆ H ₂ (NO ₂) ₃] ⁻ , (C ₃ H ₇) ₃ NH ⁺ , CH ₃ OC ₆ H ₄ - COO ⁻	7	.975	.965	.948	.930	.909	.875	.845	.81
(C ₆ H ₅) ₂ CHCOO ⁻ , (C ₃ H ₇) ₄ N ⁺	8	.975	.966	.949	.931	.912	.880	.85	.82
(COO) ₂ ²⁻ , H citrate ²⁻	4.5	.903	.867	.804	.741	.662	.55	.45	.36
H ₂ C(COO) ₂ ²⁻ , (CH ₂ COO) ₂ ²⁻ , (CHOHCOO) ₂ ²⁻	5	.903	.868	.805	.744	.67	.555	.465	.38
C ₆ H ₄ (COO) ₂ ²⁻ , H ₂ C(CH ₂ COO) ₂ ²⁻ , (CH ₂ CH ₂ - COO) ₂ ²⁻	6	.905	.870	.809	.749	.675	.57	.485	.405
[OOC(CH ₂) ₆ COO] ²⁻ , [OOC(CH ₂) ₈ COO] ²⁻ , Congo red anion ²⁻	7	.906	.872	.812	.755	.685	.58	.50	.425
Citrate ³⁻	5	.796	.728	.616	.51	.405	.27	.18	.115

As another test we have in Table III compared the experimental¹⁶ mean activity coefficients for some strong electrolytes with those calculated from individual coefficients. The last four col-

umns represent: (1) author's Table II (formula 1, with calculated a_1 -values); (2) author's approximate formulas; (3) Guggenheim's formula; and (4) Lewis and Randall's old tables.

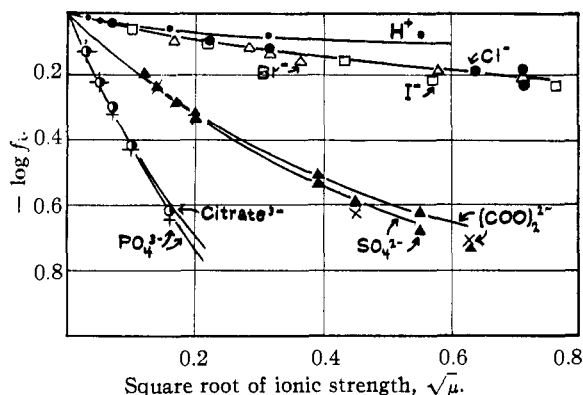


Fig. 1.—Individual activity coefficients of ions: drawn lines represent calculated values, with rounded a_i — figures given in Table I.

TABLE III

Electrolyte	Ionic concn. Γ	Mean ionic activity coefficient				
		Exptl.	Table II	Approx. formula	Guggenheim formula	Lewis-Randall tables
HI	0.01	0.927	0.928	0.927	0.927	0.95
	.02	.902	.906	.90	.90	.92
	.04	.870	.875	.865	.865	.895
	.1	.822	.83	.81	.81	.86
	.2	.787	.79	.76	.76	.815
HCl	.01	.928	.928	.927	.927	.95
	.02	.905	.906	.90	.90	.92
	.04	.878	.875	.865	.865	.895
	.1	.831	.83	.81	.81	.86
	.2	.799	.79	.76	.76	.815
HCl in LaCl ₃	.125	.818	.82	.795	.795	.85
	.15	.811	.81	.78	.78	.84
	.175	.794	.80	.77	.77	.825
NH ₄ NO ₃	.02	.882	.898	.90	.90	...
	.04	.840	.865	.87	.87	...
	.1	.783	.80	.81	.81	...

	.2	.726	.75	.76	.76	...
	.4	.658	.69	.70	.70	...
	1.0	.59	.605	.62	.62	...
LiC ₇ H ₇ SO ₃	0.04	.877	.88	.875	.87	...
	.25	.782	.785	.77	.74	...
	1.0	.703	.71	.675	.62	...
HCOONa	0.004	.954	.955	.953	.953	...
	.01	.931	.927	.927	.927	...
	.02	.908	.901	.90	.90	...
	.04	.879	.87	.865	.865	...
Li ₂ SO ₄	.012	.862	.85	.855	.85	.82
	.03	.808	.78	.79	.78	.75
	.06	.754	.725	.73	.71	.70
	.3	.601	.57	.58	.525	...
ZnCl ₂	.01	.857	.861	.865	.86	.845
	.03	.778	.78	.79	.78	.77
	.1	.660	.68	.685	.66	.67
	.17	.609	.63	.63	.59	.62
	.5	.51	.53	.53	.465	...
La(NO ₃) ₃	.0145	.796	.785	.785	.765	.79
	.034	.720	.71	.71	.675	.72
	.066	.645	.645	.645	.59	.64
	.118	.570	.59	.59	.51	.57
	.221	.505	.525	.525	.42	.50
K ₃ Fe(CN) ₆	.012	.785	.79	.79	.78	.82
	.024	.717	.72	.73	.71	.76
	.06	.618	.61	.63	.60	.69
	.12	.547	.52	.55	.51	.62

Summary

Individual activity coefficients of 130 inorganic and organic ions in water at concentrations up to $\Gamma = 0.2$ have been computed and tabulated; parameters a_i were calculated by various methods. For approximative work, these individual figures have been shown to give mean coefficients in sufficient accordance with experimental values.

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[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Constituents of Pyrethrum Flowers. IX. The Optical Rotation of Pyrethrolone and the Partial Synthesis of Pyrethrins¹

BY H. L. HALLER AND F. B. LAForge

Among the observations on the chemical and physical properties of tetrahydropyrethrolone, we have previously reported its specific rotation as $+11.9^\circ$.² This value agrees in magnitude but differs in sign from the one (-11.3°) reported by Staudinger and Ruzicka³ for the same compound.

The material on which their rotation is reported was prepared by hydrogenation of a pyrethrolone preparation obtained from a mixture of the semicarbazones of pyrethrins I and II in which the relative proportions of each were unknown.

(1) For Article VIII of this series, see *J. Org. Chem.*, **2**, 56 (1937).

(2) LaForge and Haller, *THIS JOURNAL*, **58**, 1777 (1936).

(3) Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 212 (1924).

Since the rotation reported by us was also observed on material originating from a mixture of both pyrethrins, the discrepancy between our value and that reported by Staudinger and Ruzicka might be explained with the assumption that the pyrethrolone present in pyrethrin I differed optically from the one in pyrethrin II.

We have previously described a method⁴ by which pyrethrin concentrates may be separated into fractions in each of which one of the pyrethrins predominates. From a fraction in which pyrethrin I predominates its semicarbazone may

(4) LaForge and Haller, *THIS JOURNAL*, **57**, 1893 (1935).