Canadian Mineralogist
Vol. 14, pp. 498-502 (1976)

THE GLADSTONE-DALE RELATIONSHIP — PART I: DERIVATION OF NEW CONSTANTS

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ABSTRACT

Using the data for Tutton's salts, and other pure synthetic compounds, new constants were derived for 106 constituents. For the constituents derived from Tutton's salts, the new constants are more accurate than those given by Larsen.

SOMMAIRE

De nouvelles constantes ont été établies pour 106 constituants à l'aide des données sur les sels de Tutton et autres composés synthétiques purs. Ces constantes sont plus justes que celles de Larsen.

(Traduit par la Rédaction)

INTRODUCTION

Many mathematical expressions relating refractive index, density, and chemical composition have been derived. It is not the purpose of this paper to compare these different relationships. In fact, the writer is extremely biased in favor of the Gladstone-Dale relationship because: (1) it involves a very simple calculation and (2) it affords a fairly reliable check on mineralogical data.

The Gladstone-Dale relationship was formulated by Gladstone & Dale (1864). It was introduced to mineralogists by Larsen (1921) who also derived many of the constants currently in use. The relationship is best explained by the equation

$$K = \frac{n-1}{d} = \frac{k_1 p_1}{100} + \frac{k_2 p_2}{100} + \cdots \frac{k_n p_n}{100}$$

In the equation: K is the specific refractive energy of a substance, n is its refractive index, d is its density, k_1, k_2, etc. are the specific refractive energies of its various components, p_1, p_2, etc. are the weight percentages of its components.

In applying the relationship to optically anisotropic substances, the mean refractive index $\bar{n}$ should be used. The value of $\bar{n}$ is $(2\omega+\epsilon)/3$ for uniaxial substances and $(\alpha+\beta+\gamma)/3$ for biaxial substances.

Larsen's constants for various components have been in use since 1921. Jaffe (1956) recalculated some of Larsen's constants, but found that most of them required no revision. New constants for CuO and Sc_2O_3 were proposed by Mrose (1965). Faust & Schaller (1971) gave a new constant for SnO_2. More recently Trzcienski *et al.* (1974) proposed a new constant for P_2O_5. The writer first became aware that some of Larsen's constants probably were in error while working on some tellurites and selenites in 1961. Larsen's k values for SeO_2 and TeO_2 seemed to be in error, and the k value for TeO_3 seemed incredibly high. In fact, this last constant was calculated from the very sketchy data for the poorly-defined mineral "montanite". It is not surprising that Larsen's constant for TeO_3 is about four times the value of the constant calculated in this study. Several other constants given by Larsen obviously were calculated from unsatisfactory data. Larsen (1921) himself pointed out the unreliability of some of the density values and the inadequate knowledge of the chemical compositions of certain minerals. In a preliminary study, the present writer found that a number of the constants were in error, and some of these were reported (Mandarino 1964).

The present writer decided that a complete recalculation of k values for all components should be undertaken. In order to avoid poor sets of data the following approach was taken. Calculations would start with a group of compounds which had been thoroughly studied and for which the data seemed most reliable. If possible, these compounds should be pure synthetic materials to avoid the impurities usually present in most minerals. A group of compounds which fits these requirements is "Tutton's salts". Between 1893 and 1928 Tutton studied 75 compounds of the general formula $R'_2R''(XO_4)_2 \cdot 6H_2O$, where R' is K, NH_4, Rb, Cs, or Tl; R'' is Mg, Mn, Fe, Co, Ni, Cu, Zn, or Cd; and X is S, Se, or Cr. For specific references to Tutton's papers see Winchell *et al.* (1964). These compounds provided data for the calculation of constants for 17 oxide components.

To begin the calculations it was assumed that Larsen's k values for SO_3 and H_2O were sound. The other constants were calculated by a trial

and error method. After they were calculated, they were refined by recycling the calculations until the standard deviation for each constant was relatively small. These constants were then applied to other pure synthetic compounds which contained additional components in order to calculate k values for those components. Eventually, constants for all of the usual components of minerals and for many rare components were derived. The relationships which exist among the various constants will be discussed in another part of this series.

Constants from Tutton's Salts

The constants derived from the data for Tutton's salts are given in Table 1. The differences between Larsen's constants and those obtained in this study are apparent. A test was carried out to determine which set of constants gave better results. The test consisted of calculating the specific refractive energy (K) of each of Tutton's salts three different ways. First, the K values were calculated from Tutton's measured refractive indices and densities using the relationship, $K = \frac{n-1}{d}$ where n is the mean refractive index. Then, K values were calculated using the k values of this study and the relationship, $K = \frac{k_1 p_1}{100} + \frac{k_2 p_2}{100} +$

TABLE 1. COMPARISON OF K VALUES OF THE COMPONENTS OF TUTTON'S SALTS

Component	(a) k (this study)	(b) k (Larsen 1921)	Δk (b–a)
H_2O	0.340	0.340 average	—
$(NH_4)_2O$	0.483	0.503	+0.020
K_2O	0.196	0.189	-0.007
Rb_2O	0.128	0.129	+0.001
Cs_2O	0.119	0.124	+0.005
Tl_2O	0.115	0.120	+0.005
MgO	0.225*	0.200	-0.025
MnO	0.197	0.191	-0.006
FeO	0.188	0.187	-0.001
CoO	0.179	0.184	+0.005
NiO	0.176	0.184	+0.008
CuO	0.170	0.191	+0.021
ZnO	0.158	0.153	-0.005
CdO	0.130	0.134	+0.004
SO_3	0.177	0.177	—
CrO_3	0.335	0.36	+0.025
SeO_3	0.164	0.165	+0.001

* This value for MgO should be used only for sulfates.

TABLE 2. COMPARISON OF K VALUES FOR TUTTON'S SALTS

Compound $R'_2R''(XO_4)_2 \cdot 6H_2O$			Calculated K			ΔK	ΔK
R'	R''	X	(a) Tutton obs. data	(b) from k, this study	(c) from Larsen k	(a–b)	(a–c)
K	Mg	S	0.2297	0.2299	0.2258	-0.0002	0.0039
K	Fe	S	0.2235	0.2235	0.2233	0.0000	0.0002
K	Co	S	0.2214	0.2217	0.2210	-0.0003	0.0004
K	Ni	S	0.2213	0.2212	0.2210	0.0001	0.0003
K	Cu	S	0.2200	0.2197	0.2220	0.0003	-0.0020
K	Zn	S	0.2169	0.2173	0.2149	-0.0004	0.0020
NH_4	Mg	S	0.2758	0.2757	0.2754	0.0001	0.0004
NH_4	Mn	S	0.2651	0.2664	0.2680	-0.0013	-0.0029
NH_4	Fe	S	0.2648	0.2645	0.2669	0.0003	-0.0021
NH_4	Co	S	0.2612	0.2623	0.2659	-0.0011	-0.0047
NH_4	Ni	S	0.2611	0.2618	0.2659	-0.0007	-0.0048
NH_4	Cu	S	0.2586	0.2594	0.2662	-0.0008	-0.0076
NH_4	Zn	S	0.2558	0.2566	0.2582	-0.0008	-0.0024
NH_4	Cd	S	0.2378	0.2383	0.2418	-0.0005	-0.0040
Rb	Mg	S	0.1980	0.1979	0.1963	0.0001	0.0017
Rb	Mn	S	0.1962	0.1958	0.1952	0.0004	0.0010
Rb	Fe	S	0.1940	0.1945	0.1948	-0.0005	-0.0008
Rb	Co	S	0.1926	0.1932	0.1943	-0.0006	-0.0017
Rb	Ni	S	0.1926	0.1928	0.1942	-0.0002	-0.0016
Rb	Cu	S	0.1923	0.1917	0.1952	0.0006	-0.0029
Rb	Zn	S	0.1898	0.1899	0.1894	-0.0001	0.0004
Rb	Cd	S	0.1822	0.1811	0.1823	0.0011	-0.0001
Cs	Mg	S	0.1827	0.1824	0.1830	0.0003	-0.0003
Cs	Mn	S	0.1817	0.1813	0.1829	0.0004	-0.0012
Cs	Fe	S	0.1801	0.1803	0.1825	-0.0002	-0.0024
Cs	Co	S	0.1793	0.1794	0.1822	-0.0001	-0.0029
Cs	Ni	S	0.1786	0.1789	0.1821	-0.0003	-0.0035
Cs	Cu	S	0.1779	0.1781	0.1831	-0.0002	-0.0052
Cs	Zn	S	0.1761	0.1765	0.1780	-0.0004	-0.0019
Cs	Cd	S	0.1693	0.1699	0.1728	-0.0006	-0.0035
Tl	Mg	S	0.1638	0.1678	0.1693	-0.0040	-0.0055
Tl	Mn	S	0.1623	0.1674	0.1696	-0.0051	-0.0073
Tl	Fe	S	0.1661	0.1667	0.1693	-0.0006	-0.0032
Tl	Co	S	0.1625	0.1658	0.1691	-0.0033	-0.0066
Tl	Ni	S	0.1632	0.1654	0.1690	-0.0022	-0.0058
Tl	Cu	S	0.1634	0.1649	0.1699	-0.0015	-0.0065
Tl	Zn	S	0.1630	0.1637	0.1659	-0.0007	-0.0029
K	Mg	Se	0.2133	0.2138	0.2109	-0.0005	0.0024
K	Fe	Se	0.2091	0.2090	0.2080	0.0001	0.0011
K	Co	Se	0.2076	0.2076	0.2075	0.0000	0.0001
K	Ni	Se	0.2068	0.2073	0.2075	-0.0005	-0.0007
K	Cu	Se	0.2057	0.2060	0.2082	-0.0003	-0.0025
K	Zn	Se	0.2044	0.2040	0.2026	0.0004	0.0018
NH_4	Mg	Se	0.2481	0.2479	0.2484	0.0002	-0.0003
NH_4	Mn	Se	0.2415	0.2423	0.2440	-0.0008	-0.0025
NH_4	Fe	Se	0.2417	0.2409	0.2433	0.0008	-0.0016
NH_4	Co	Se	0.2392	0.2391	0.2426	0.0001	-0.0034
NH_4	Ni	Se	0.2398	0.2387	0.2425	0.0011	-0.0027
NH_4	Cu	Se	0.2392	0.2372	0.2432	0.0020	-0.0040
NH_4	Zn	Se	0.2349	0.2350	0.2367	-0.0001	-0.0018
NH_4	Cd	Se	0.2152	0.2217	0.2245	-0.0065	-0.0093
Rb	Mg	Se	0.1888	0.1890	0.1880	-0.0002	0.0008
Rb	Mn	Se	0.1871	0.1875	0.1876	-0.0004	-0.0005
Rb	Fe	Se	0.1864	0.1866	0.1871	-0.0002	-0.0007
Rb	Co	Se	0.1857	0.1855	0.1868	0.0002	-0.0011
Rb	Ni	Se	0.1850	0.1852	0.1868	-0.0002	-0.0018
Rb	Cu	Se	0.1837	0.1843	0.1877	-0.0006	-0.0040
Rb	Zn	Se	0.1832	0.1827	0.1827	0.0005	0.0005
Cs	Mg	Se	0.1768	0.1769	0.1779	-0.0001	-0.0011
Cs	Mn	Se	0.1757	0.1761	0.1778	-0.0004	-0.0021
Cs	Fe	Se	0.1756	0.1753	0.1775	0.0003	-0.0019
Cs	Co	Se	0.1748	0.1745	0.1772	0.0003	-0.0024
Cs	Ni	Se	0.1751	0.1741	0.1771	0.0010	-0.0020
Cs	Cu	Se	0.1734	0.1735	0.1780	-0.0001	-0.0046
Cs	Zn	Se	0.1720	0.1719	0.1738	0.0001	-0.0018
Tl	Mg	Se	0.1702	0.1649	0.1664	0.0053	0.0038
Tl	Mn	Se	0.1674	0.1646	0.1668	0.0028	0.0006
Tl	Fe	Se	0.1646	0.1639	0.1666	0.0007	-0.0020
Tl	Co	Se	0.1631	0.1632	0.1663	-0.0001	-0.0032
Tl	Ni	Se	0.1624	0.1630	0.1665	-0.0006	-0.0041
Tl	Cu	Se	0.1665	0.1625	0.1671	0.0040	-0.0006
Tl	Zn	Se	0.1647	0.1614	0.1637	0.0033	0.0010
NH_4	Mg	Cr	0.3509	0.3445	0.3570	0.0064	-0.0061
Rb	Mg	Cr	0.2562	0.2554	0.2632	0.0008	-0.0070
Cs	Mg	Cr	0.2344	0.2322	0.2409	0.0022	-0.0065

Calculated K: (a) from Tutton's observed data; (b) calculated from k values of this study; (c) calculated from Larsen's (1921) k values.

$\frac{k_n p_n}{100}$. Finally, Larsen's k values were used in the last equation to calculate K values. Table 2 compares the three K values for each compound.

A quick examination of Table 2 shows that, in general, the K values calculated from Larsen's constants depart from the "observed" K values more than do the K values calculated from the constants derived in this study. This is not surprising since the latter constants were calculated from the data of these particular compounds. However, to continue the comparison, in 67 of the compounds (89%) Larsen's constants gave K values farther from the "observed" K values than did the constants from this study. The average "error" using Larsen's constants is 0.0027 compared to 0.0010 using the constants of this study. If all the figures in Table 2 are expressed to only three decimal places, as is normal, Larsen's values still give a greater "error" in 58 compounds (77%). The average "error" for Larsen's constants is 0.003 compared to 0.001 for the constants of this study.

Figure 1 illustrates some points that are not readily apparent from Table 2. In Figure 1, Larsen's "errors" have been plotted against the "errors" from this study. Of the 75 K values

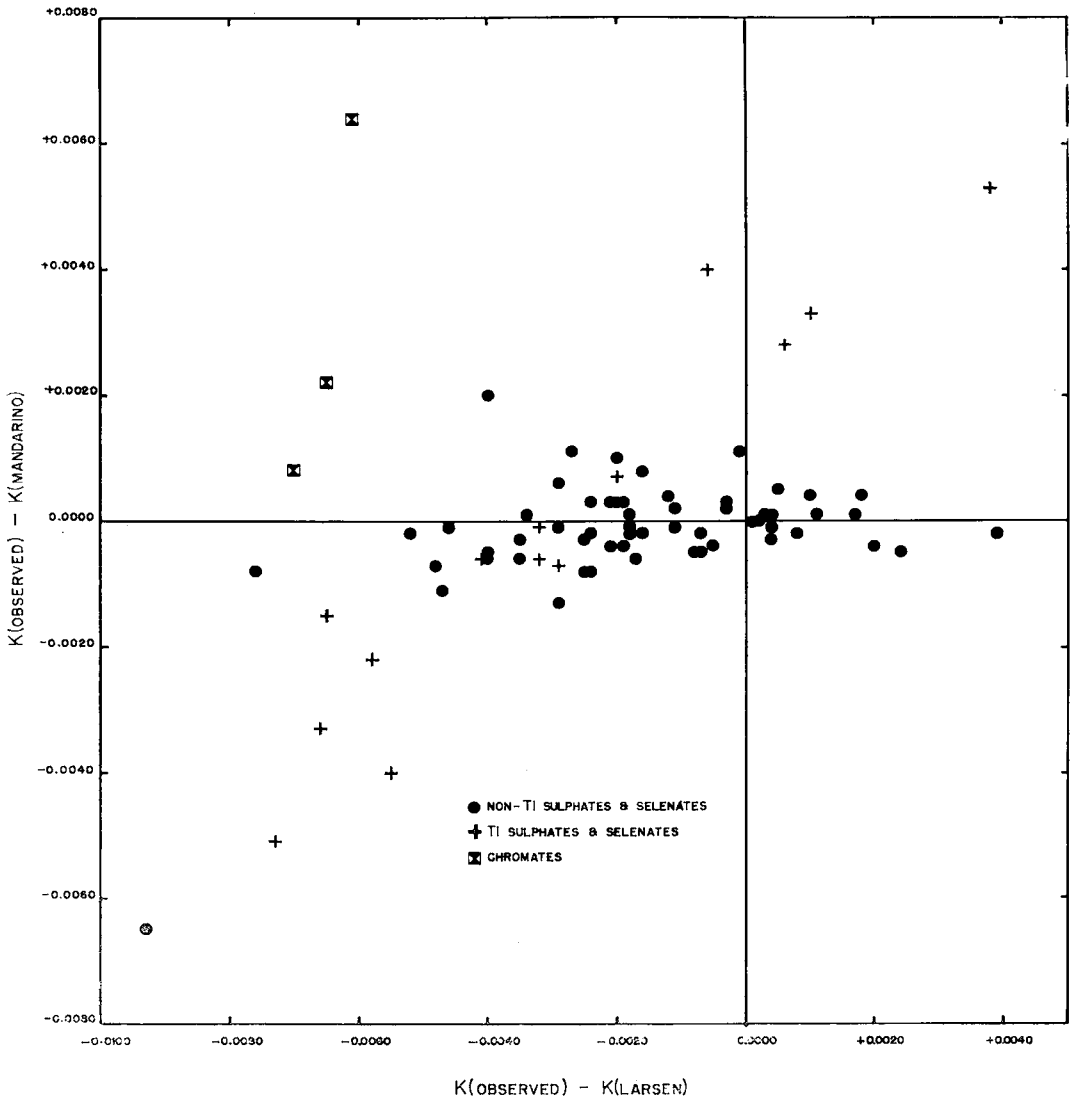

FIG. 1. Comparison of K(Observed) – K(Larsen) and K(Observed) – K(Mandarino) for Tutton's salts.

TABLE 3. GLADSTONE-DALE CONSTANTS*

Component	At. no.	Molecular wt.	k This study	k Larsen (1921)	k Others†
H_2O	1	18.02	0.340	0.340 average 0.3355 water & ice 0.354 alums, *etc.*	
Li_2O	3	29.88	0.307	0.31	
$(NH_4)_2O$	-	52.08	0.483	0.503	
Na_2O	11	61.98	0.190	0.181	
K_2O	19	94.20	0.196	0.189	
Cu_2O	29	143.09	0.234	0.250	
Rb_2O	37	186.94	0.128	0.129	
Ag_2O	47	231.74	0.168	0.154	
Cs_2O	55	281.81	0.119	0.124	
Hg_2O	80	417.18	0.144	0.169 (Li)	
Tl_2O	81	424.74	0.115	0.120	
BeO	4	25.01	0.240	0.238	
MgO	12	40.30	0.200 0.225 sulfates	0.200	
CaO	20	56.08	0.210	0.225	
VO	23	66.94	(0.207)		
CrO	24	68.00	(0.202)		
MnO	25	70.94	0.197	0.191 compounds 0.224 oxide	
FeO	26	71.85	0.188	0.187	
CoO	27	74.93	0.179	0.184	
NiO	28	74.71	0.176	0.184	
CuO	29	79.55	0.170	0.191 compounds 0.235 (Li) oxide	0.173[M]
ZnO	30	81.37	0.158	0.153 compounds 0.183 oxide	
SrO	38	103.62	0.145	0.143	
CdO	48	128.40	0.130	0.134	
SnO	50	134.69	(0.140)		
BaO	56	153.34	0.128	0.127	
HgO	80	216.59	0.123	0.18	
PbO	82	223.19	0.133	0.137 compounds 0.175 (Li) oxide	
B_2O_3	5	69.62	0.215	0.220 isom. oxide	
C_2O_3	6	72.02	0.270	0.265	
N_2O_3	7	76.01	(0.325)		
Al_2O_3	13	101.96	0.207 0.242 sulfates	0.193 0.214 feldspars, *etc.*	
P_2O_3	15	109.95	(0.315)		
Sc_2O_3	21	137.91	0.257		0.248[J] 0.264[M]
Ti_2O_3	22	143.80	(0.267)		
V_2O_3	23	149.88	(0.279)		
Cr_2O_3	24	151.99	(0.290)	0.27	
Mn_2O_3	25	157.87	0.301	0.300 compounds 0.304 (Li) oxide	
Fe_2O_3	26	159.69	0.315	0.308 compounds	0.290[J] silicates
			0.268 silicates	0.36 (Li) oxide	0.310[J] hyd. sulf. 0.404[J] oxide
Co_2O_3	27	165.86	(0.329)		
Ni_2O_3	28	165.42	(0.339)		
Ga_2O_3	31	187.44	0.170		
As_2O_3	33	197.84	0.235	0.202 isom. oxide 0.225 monocl. oxide	
Y_2O_3	39	225.81	0.170	0.144	0.170[J]
In_2O_3	49	277.64	0.130		
Sb_2O_3	51	291.50	0.203	0.209 isom. oxide 0.232 ortho. oxide	
La_2O_3	57	325.82	0.148	0.149	0.142[J]
Ce_2O_3	58	328.24	0.144	0.16	0.149[J]
Pr_2O_3	59	329.81	0.141		0.140[J]
Nd_2O_3	60	336.48	0.137		0.133[J]
Pm_2O_3	61	342	(0.133)		
Sm_2O_3	62	348.70	0.130		0.141[J]
Eu_2O_3	63	351.92	0.126		
Gd_2O_3	64	362.50	0.123		
Tb_2O_3	65	365.85	0.119		
Dy_2O_3	66	373.00	0.115		
Ho_2O_3	67	377.86	0.112		
Er_2O_3	68	382.52	0.108		
Tm_2O_3	69	385.87	0.104		
Yb_2O_3	70	394.08	0.101		
Lu_2O_3	71	397.94	0.097		
Tl_2O_3	81	456.74	0.053		
Bi_2O_3	83	465.96	0.153	0.163	
CO_2	6	44.01	0.211	0.217	
SiO_2	14	60.08	0.208	0.207	
SO_2	16	64.06	0.262		
TiO_2	22	79.90	0.393	0.397	
VO_2	23	82.94	0.393		
CrO_2	24	83.99	(0.394)		
MnO_2	25	86.94	0.394		
GeO_2	32	104.59	0.167		
SeO_2	34	110.96	0.203	0.147	
ZrO_2	40	123.22	0.211	0.201	
SnO_2	50	150.69	0.143	0.145	0.132[F]
TeO_2	52	159.60	0.183	0.200 (Li) oxide	
HfO_2	72	210.49	0.115		
PbO_2	82	239.19	0.105		
ThO_2	90	264.04	0.167	0.12	
N_2O_5	7	108.01	0.242	0.240	
P_2O_5	15	141.94	0.176	0.190	0.170[T]
Cl_2O_5	17	150.90	0.220	0.218	
V_2O_5	23	181.88	0.340	0.43	
As_2O_5	33	229.84	0.162	0.169	
Br_2O_5	35	239.81	0.180	0.183	
Nb_2O_5	41	265.81	0.268	0.295	
Sb_2O_5	51	323.50	(0.153)	0.152 0.222 (?)	
I_2O_5	53	333.81	0.195	0.177	
Ta_2O_5	73	441.89	0.151	0.133	
Bi_2O_5	83	497.96	(0.139)		
SO_3	16	80.06	0.177	0.177	
CrO_3	24	99.99	0.335	0.36	
SeO_3	34	126.96	0.164	0.165	
MoO_3	42	143.94	0.237	0.241 (Li)	0.234[J]
TeO_3	52	175.60	0.157	0.607	
WO_3	74	231.85	0.152	0.133	
UO_3	92	286.03	0.118	0.134	
S_2O_7	16	176.12	0.133		
Cl_2O_7	17	182.90	0.182		
Mn_2O_7	25	221.87	0.348		
Br_2O_7	35	271.80	(0.156)		
I_2O_7	53	365.80	0.168		
F^{-1}	9	19.00	0.047	0.043	
Cl^{-1}	17	35.45	0.318	0.303	
Br^{-1}	35	79.90	0.217	0.214	
I^{-1}	53	126.90	0.227	0.226	
O^{-2}	8	16.00	0.203	0.203	

* Constants given in brackets, such as VO (0.207) were derived either by extrapolation or by interpolation.
† M = Mrose (1965); J = Jaffe (1956); T = Trzcienski *et al.* (1974); F = Faust (1971).

calculated from Larsen's constants only 19 (25%) are within ±0.001 of the observed values, 37 (49%) are within ±0.002, and 38 (51%) differ from the observed values by more than 0.002. Of the K values calculated from the constants derived in this study, 58 (77%) are within ±0.001 of the observed values, 64 (85%) are within ±0.002, and only 11 (15%) differ by more than 0.002.

The data for the thallium compounds show much greater errors than do the data for the other compounds. Analysis of these data indicated that some of Tutton's observed data for the thallium compounds might be in error. This is discussed in another part of this series.

The New Constants

In addition to the 17 constants derived from the data of Tutton's salts, numerous other constants were calculated. Most of these were calculated from the data of pure synthetic compounds. Several constants were determined by interpolation and extrapolation after certain relationships among constants became apparent. A total of 109 constants for 106 constituents is given in Table 3. Of these, 15 constants were derived by interpolation or extrapolation. In addition to the constants derived in this study, Table 3 contains the following additional data: the atomic numbers of the elements of the components, the molecular weights of the components, Larsen's k values and the k values proposed by other writers.

In subsequent parts of this series, the following subjects will be covered: the relationships which exist among various constants, the evidence which supports the greater accuracy of the new constants, and some special applications of the Gladstone-Dale relationship.

Acknowledgements

Much of the work that went into the derivation of these constants took place while I was on a National Research Council of Canada Senior Research Fellowship in France. I am grateful to the NRC for the fellowship and to Dr. Claude Guillemin who allowed me to spend my fellowship at the B.R.G.M. in Orléans. My special thanks go to Dr. Roland Pierrot of the B.R.G.M. who was most helpful and encouraging during this project. My thanks also go to Miss Helen Driver who typed the manuscript and especially to Mrs. J. Galt who spent many hours typing the tables.

References

Faust, G. T. & Schaller, W. T. (1971): Schoenfliesite, $MgSn(OH)_6$. *Z. Krist.* **134**, 116-141.

Gladstone, J. H. & Dale, T. P. (1864): Researches on the refraction, dispersion, and sensitiveness of liquids. *Philos. Trans. Roy. Soc. London* **153**, 317-343.

Jaffe, H. W. (1956): Application of the rule of Gladstone and Dale to minerals. *Amer. Mineral.* **41**, 757-777.

Larsen, E. S. (1921): The microscopic determination of the nonopaque minerals. *U. S. Geol. Surv. Bull.* **679**.

——— & Berman, H. (1934): The microscopic determination of the nonopaque minerals. *U.S. Geol. Surv. Bull.* **848**.

Mandarino, J. A. (1964): Critical analysis of the Gladstone-Dale rule and its constants. *Can. Mineral.* **8**, 137 (Abstr.).

Mrose, M. E. (1965): New specific refractive energy values for CuO and Sc_2O_3. *Amer. Mineral.* **50**, 288 (Abstr.).

Trzcienski, W. E. jr., Perrault, G. & Hebert, P. (1974): A note on apatite from Huddersfield Township, Quebec. *Can. Mineral.* **12**, 289-291.

Winchell, A. N. & Winchell, H. (1964): *The Microscopic Characters of Artificial Inorganic Solid Substances: Optical Properties of Artificial Minerals.* Academic Press, New York.

Manuscript received March 1976, emended May 1976.