Chemistry. — "*Investigations on the Temperature-coefficients of the Free Molecular Surface-Energy of Liquids between* —80° and 1650° C.": **XVII.** *The relations between the Molecular Cohesion of Liquids at their Melting- and Boilingpoints, and their absolute Melting- and Boiling-temperatures respectively*". By Prof. Dr. F. M. JAEGER.

(Communicated in the meeting of June 24, 1916.)

§ **1.** Some eight years ago already P. WALDEN[1]) drew attention in a number of interesting papers to the remarkable empirical relations, which seem to be present between the capillary constants of non-associated liquids at their boiling- and meltingpoint, and these temperatures themselves, if expressed in terms of the absolute scale.

Starting from the empirically stated rule, according to which the quotient of the heat of evaporisation and of the specific cohesion at the boilingpoint: $\frac{Q}{a^2_b}$, oscillates closely about a mean value of **17,9**, if the liquids are not appreciably associated, — he found by combination of this rule with the so-called "rule of TROUTON", according to which in the case of normal liquids the quotient of the molecular heat of evaporisation and of the absolute boiling-temperature: $\frac{Q}{T_b}$ should be a constant (ω **20,7**), — the relation:

$$\frac{Ma^2_b}{T_b} \omega \text{ 1,156.}$$

By analogous reasoning WALDEN found also for substances at their meltingpoint a similar relation; the mean value, round which the said quotient oscillates, should in the case of non-associated liquids, be: **3,65**. For associated liquids, however, both mean values should be appreciably *smaller*. Both, of course only approximative empirical rules, may be formulated as follows:

At the melting- and boilingpoint of the substances the quotients of the molecular cohesion and the absolute melting-, respectively boiling-temperatures themselves, are almost constant for non-associated liquids.

WALDEN checked these conclusions by means of a number of cases, collected from literature; and he found them really confirmed, at least within certain limits. However, in the case of the inorganic salts no such mean value could be derived from the older data in literature.

§ **2.** It seemed interesting to test these relations once more by

[1]) P. WALDEN, Zeits. f. phys. Chemie **65**, 257 (1909); Zeits. f. Elektrochem. **14** 713, (1908).

§ 3. FIRST GROUP.

Chemical Compound:	Absolute Melting-temperature:	Specific Cohesion a^2 at the Meltingpoint:	K_m:	Absolute Boiling-temperature: ($p = 1$ atm.)	Spec fic Cohesion a^2 at the Boilingpoint:	K_b:
Chloroform	213°	4.79	**2.69**	334.2°	3.14	**1.12**
Carbon tetrachloride	253	3.77	**2.05**	349.4	2.72	**1.20**
Ethylene chloride	238	6.04	**2.51**	359	3.99	**1.08**
Ethylidene chloride	176.4	5.78	**3.24**	333.9	3.56	**1.05**
Ethyliodide	162.1	3.87	**3.64**	345.5	2.49	**1.10**
Acetylene tetrachloride	229	5.19	**3.80**	419.5	2.94	**1.18**
Acetylene tetrabromide	270	3.47	**4.44**	—	—	—
Isobutylbromide	—	—	—	363.5	3.08	**1.16**
Carbonbisulphide	161.4	7.00	**3.30**	319.8	4.54	**1.08**
Glycerol	292	ca. 11	**3.3**	563	6.78	**1.11**
Diethylether	156.8	8.20	**3.88**	307.8	4.65	**1.12**
Trichloroacetic Acid	330.5	3.71	**1.82**	468	2.64	**0.92**
Ethylchloroformiate	—	—	—	364.5	3.88	**1.15**
Ethylacetate	189.6	7.58	**3.52**	350.1	4.26	**1.07**
Amylacetate	—	—	—	421.4	3.82	**1.18**
Methylisobutyrate	—	—	—	364.8	4.20	**1.18**
Ethylisobutyrate	—	—	—	383.2	3.75	**1.14**
Isobutylisobutyrate	—	—	—	420.2	3.37	**1.16**
Glyceryltriformiate	291	7.42	**4.49**	539	3.17	**1.03**
Ethyl-acetyloacetate	—	—	—	452.6	3.83	**1.10**
Ethyl-propylacetyloacetate	—	—	—	496.6	3.30	**1.14**
Methylcyanoacetate	—	—	—	476	4.33	**0.90**
Ethylcyanoacetate	250.5	7.45	**3.36**	479	4.18	**0.99**
Propylcyanoacetate	234	7.57	**4.11**	489	3.96	**1.03**
Butylcyanoacetate	—	—	—	503.5	4.20	**1.18**
Isobutylcyanoacetate	247	6.82	**3.90**	496	3.69	**1.05**
Amylcyanoacetate	—	—	—	513.2	3.98	**1.20**
Diethyloxalate	232.5	6.78	**4.26**	458	3.31	**1.06**
Diethylmalonate	223	6.98	**5.01**	470.8	3.23	**1.09**
Dimethylsuccinate	291.2	6.29	**3.16**	468.3	3.31	**1.03**
Diethyltartrate	288	6.50	**4.67**	553	3.14	**1.16**
Acetone	278.7	6.24	**1.30**	329	5.22	**0.92**

FIRST GROUP, (continued).

Chemical Compound:	Absolute Melting-temperature:	Specific Cohesion a^2 at the Meltingpoint:	K_m:	Absolute Boiling-temperature: ($p = 1$ atm.)	Specific Cohesion a^2 at the Boilingpoint:	K_b:
Acetylacetone	243°	6.99	**2.86**	410.5°	4.28	**1.04**
Methylpropylcetone	189.5	7.88	**3.58**	375.3	4.45	**1.02**
Trimethylamine	—	—	—	270	5.21	**1.14**
Diethylamine	234.1	6.44	**2.01**	329	4.74	**1.05**
Triethylamine	158.3	8.20	**5.24**	362	4.00	**1.12**
norm. Propylamine	—	—	—	320.5	5.16	**0.95**
Dipropylamine	228	7.28	**3.23**	383.5	4.04	**1.07**
Isopropylamine	—	—	—	308	4.80	**0.92**
Allylamine	—	—	—	327	5.65	**0.99**
norm. Butylamine	227	7.27	**2.34**	351	4.80	**1.00**
Isobutylamine	—	—	—	341	5.00	**1.07**
Diisobutylamine	—	—	—	415	3.53	**1.10**
3^{ar} Butylamine	219	6.63	**2.21**	317	4.56	**1.05**
norm. Amylamine	235	6.90	**2.56**	377	4.58	**1.06**
Isoamylamine	—	—	—	370	4.55	**1.07**
Diisoamylamine	229	7.19	**4.94**	461	3.17	**1.08**
3^{ar} Amylamine	—	—	—	349.5	4.37	**1.09**
norm. Hexylamine	254	7.14	**2.84**	403	4.94	**1.24**
Isohexylamine	—	—	—	397	4.84	**1.23**
norm. Heptylamine	255	6.96	**3.14**	427	4.28	**1 15**
Capronitrile	228	7.08	**2.95**	430	4.19	**0.94**
Benzene	278.4	7.04	**1.97**	353.5	5.22	**1.15**
Cyclohexane	281	7.37	**2.21**	353.7	4.74	**1.13**
Toluene	178.5	ca. 10	**5**	382.4	5.09	**1.23**
p-Xylene	288	7.14	**2.63**	409.2	4.67	**1.21**
Mesitylene	227	7.84	**4.15**	435.8	4.26	**1.17**
Pseudocumene	212.5	8.07	**4.56**	441.5	4.45	**1.21**
Triphenylmethane	365	7.26	**4.86**	—	—	—
Nitrobenzene	276	7.47	**3.36**	482	4.48	**1.07**
o-Dinitrobenzene	390	6.09	**2.62**	—	—	—
m-Dinitrobenzene	364	6.38	**2.95**	565	4.69	**1.39**

FIRST GROUP, (continued).

Chemical Compound:	Absolute Melting-temperature:	Specific Cohesion a^2 at the Meltingpoint:	K_m:	Absolute Boiling-temperature: ($p = 1$ atm.)	Specific Cohesion a^2 at the Boilingpoint:	K_b:
Azoxybenzene	309°	7.22	**4.63**	—	—	—
m-Fluoronitrobenzene	272	6.08	**3.15**	470.5°	3.80	**1.14**
p-Fluoronitrobenzene	299.5	5.87	**2.76**	477	3.50	**1.03**
Chlorobenzene	308	5.91	**2.16**	404	3.92	**1.09**
m-Dichlorobenzene	254	6.29	**3.64**	445.5	4.00	**1.32**
p-Dichlorobenzene	325	4.92	**2.22**	446.5	3.56	**1.17**
o-Chloronitrobenzene	306	6.22	**3.20**	514	3.65	**1.12**
m-Chloronitrobenzene	317.5	6.01	**2.98**	509	3.66	**1.13**
p-Chloronitrobenzene	356	5.50	**2.43**	507	3.81	**1.18**
1-2-4-Chlorodinitrobenzene	324	6.26	**3.91**	—	—	—
1-2-Dichloro-4-Nitro-benzene	316	5.51	**3.35**	—	—	—
1-3-Dichloro-4-Nitro-benzene	307	5.68	**3.55**	—	—	—
1-4-Dichloro-2-Nitro-benzene	328	5.41	**3.17**	540	3.14	**1.12**
Bromobenzene	243	5.75	**3.71**	427	3.29	**1.21**
p-Fluorobromobenzene	—	—	—	423	3.09	**1.28**
o-Bromonitrobenzene	316	5.17	**3.30**	531.5	3.13	**1.19**
m-Bromonitrobenzene	329.5	5.00	**3.06**	524	3.24	**1.25**
p-Dibromobenzene	362	3.60	**2.34**	489	2.48	**1.20**
Jodobenzene	247	4.47	**3.69**	461.5	2.29	**1.01**
o-Jodonitrobenzene	323	4.62	**3.56**	—	—	—
m-Jodonitrobenzene	309	4.76	**3.84**	—	—	—
o-Nitrotoluene	269	7.55	**3.85**	491	3.80	**1.06**
p-Nitrotoluene	330.5	6.56	**2.72**	509	3.88	**1.05**
o-Bromotoluene	246	5.41	**3.76**	452	3.06	**1.16**
m-Fluorotoluene	—	—	—	387.5	4.43	**1.26**
p-Chlorotoluene	280.5	6.61	**2.98**	435.5	4.43	**1.29**
Phenol	314	7.11	**2.13**	453.5	4.73	**0.98**
o-Nitrophenol	318	6.09	**2.66**	487.5	3.54	**1.01**
m-Nitrophenol	369	6.46	**2.43**	—	—	—
p-Nitrophenol	386	6.98	**2.51**	—	—	—
1-2-4-Dinitrophenol	387	5.94	**2.83**	—	—	—
2-4-6-Trichlorophenol	342.5	4.98	**2.27**	519	3.17	**1.21**

FIRST GROUP, (continued).

Chemical Compound:	Absolute Melting-temperature:	Specific Cohesion a^2 at the Meltingpoint:	K_m:	Absolute Boiling-temperature: ($p = 1$ atm.)	Specific Cohesion a^2 at the Boilingpoint:	K_b:
Thymol	324.5°	6.49	**3.00**	504.5°	4.10	**1.32**
Anisol	236	8.10	**3.71**	424.7	4.67	**1.18**
o-Nitro-anisol	283	8.04	**4.35**	545	3.23	**0.91**
p-Nitroanisol	328	6.90	**3.22**	532	4.04	**1.16**
Phenetol	240	7.59	**3.86**	441	4.29	**1.19**
p-Nitrophenetol	333	6.47	**3.25**	556	3.80	**1.14**
o-Cresol	303	6.97	**2.49**	463.2	4.43	**1.03**
p-Cresol	310	6.69	**2.33**	473	4.15	**0.95**
Anethol	294.5	7.53	**3.79**	503.5	4.26	**1.25**
Guajacol	295	7.74	**3.15**	—	—	—
Resorcinoldimethylether	221	8.57	**5.4**	487.5	4.45	**1.26**
Hydroquinonedimethylether	329	6.97	**2.93**	—	—	—
Veratrol	295	7.44	**3.48**	479	4.42	**1.27**
4-5-Dinitroveratrol	403.5	6.31	**3.57**	—	—	—
Methylbenzoate	260.5	7.83	**4.09**	468.2	4.41	**1.28**
Ethylbenzoate	239	7.55	**4.74**	483.8	3.84	**1.19**
Methylsalicylate	264.5	7.20	**4.14**	496	3.87	**1.19**
Ethylsalicylate	263	7.01	**4.43**	504.2	3.75	**1.24**
Salol	315	7.27	**4.94**	—	—	—
Methylcinnamylate	309.5	7.52	**3.94**	526.5	4.20	**1.29**
Ethylcinnamylate	279.5	7.36	**4.64**	543	3.62	**1.18**
Acetophenone	293.5	8.09	**3.31**	474.5	5.30	**1.34**
Salicylaldehyde	266	7.86	**3.61**	465.5	5.01	**1.31**
Anisaldehyde	275.5	7.98	**3.94**	520	4.26	**1.11**
Benzophenone	321.5	7.54	**4.27**	578	4.24	**1.01**
2-4-2'-4'-Tetrachlorobenzophenone-dichloride	413	4.48	**4.07**	—	—	—
Aniline	267	9.00	**3.14**	457	5.70	**1.16**
m-Nitroaniline	385	7.35	**2.63**	559	5.23	**1.29**
o-Chloroaniline	273	7.18	**3.35**	483.5	4.76	**1.25**
p-Chloroaniline	343	6.68	**2.48**	505	4.82	**1.22**
Monomethylaniline	216	8.94	**4.43**	468.5	5.03	**1.15**

FIRST GROUP, (continued).

Chemical Compound:	Absolute Melting-temperature:	Specific Cohesion a^2 at the Meltingpoint:	K_m:	Absolute Boiling-temperature: ($p = 1$ atm.)	Specific Cohesion a^2 at the Boilingpoint:	K_b:
p-Nitro-monomethylaniline	425°	7.89	**2.82**	—	—	—
Dimethylaniline	273.5	8.35	**3.69**	4.92°	464	**1.28**
Diisobutylaniline	—	—	—	3.00	523	**1.18**
o-Toluidine	250	9.07	**3.89**	4.84	470.4	**1.10**
3-Nitro-o-toluidine	369	6.80	**2.80**	—	—	—
5-Nitro-o-toluidine	401	7.97	**3.02**	—	—	—
3-Nitro-p-toluidine	390	6.40	**2.50**	—	—	—
Diphenylamine	327	7.56	**3.93**	—	—	—
Pyridine	221	8.73	**2.97**	387.5	5.78	**1.12**
Piperidine	264	7.23	**2.33**	381	4.90	**1.09**
γ-Picoline	209	9.18	**4.09**	406.5	5.30	**1.21**
Chinoline	250.4	8.93	**4.60**	506	5.00	**1.28**
Sylvestrene	—	—	—	450	2.98	**0.90**
Terebene	—	—	—	443	3.78	**1.16**
Furfurol	242	7.80	**3.10**	435	5.04	**1.11**
Thiophene	234	6.80	**2.35**	360	4.71	**1.10**
Epichlorohydrine	225	7.28	**2.98**	390	4 68	**1.11**
SECOND GROUP.						
Water	273°	15.48	**1.02**	373°	12.44	**0.60**
Methylalcool	176	7.22	**1.31**	338.5	5.09	**0.48**
Ethylalcool	159	7.59	**2.20**	351.4	4.70	**0.61**
norm. Propylalcool	—	—	—	369.7	4.84	**0.79**
Isobutylalcool	—	—		379.8	4.61	**0.89**
Formic Acid	279	6.31	**1.04**	374	5.29	**0.65**
Acetic Acid	289.8	5.40	**1.12**	391.1	3.72	**0.57**
Monochloroacetic Acid	335.5	5.14	**1.45**	460	3.77	**0.78**
Dichloroacetic Acid	283	4.79	**2.16**	465.5	3.04	**0.84**
Ethylformiate	192.5	7.56	**1.97**	327.3	4.69	**0.72**
Methylamine	—	—	—	267	6.31	**0.73**
Dimethylamine	—	—	—	280.5	5.30	**0.85**

SECOND GROUP, (continued).

Chemical Compound.	Absolute Melting-temperature:	Specific Cohesion a^2 at the Meltingpoint:	K_m	Absolute Boiling-temperature: ($p = 1$ atm.)	Specific Cohesion a^2 at the Boilingpoint:	K_b
Ethylamine	189°.2	7.75	**1.85**	293°	5.76	**0.89**
Tripropylamine	—	—	—	430	3.35	**0.79**
Formamide	268	10.5	**1.76**	468	8.1	**0.78**
Nitromethane	249	6.86	**1.64**	375	4.98	**0.81**
THIRD GROUP.						
Glyceryltriacetate	—	—	—	533°	3.28	**1.34**
Glyceryltributyrate	—	—	—	559	3.02	**1.63**
Glyceryltricaprylate	282°	6.33	**10.6**	—	—	—
Glyceryltricaproate	213	6.75	**12.2**	—	—	—
Glyceryltricaprinate	304.1	6.13	**11.4**	—	—	—
Glyceryltrilaurinate	319.5	6.84	**13.5**	—	—	—
Glyceryltripalmitate	338.1	7.06	**16.7**	—	—	—
Glyceryltristearate	344.6	7.09	**17.7**	—	—	—
Glyceryltrioleate	ca. 256	8.6	**29.7**	—	—	—
Dimethyltartrate	321	6.71	**3.72**	553	4.57	**1.47**
Levulinic Acid	306	7.06	**2.68**	426.5	5.90	**1.60**
Nitrosomethylaniline	286°	8.00	**3.81**	401	6.48	**2 19**
Benzylbenzoate	286	7.93	**5.88**	581	5.17	**1.89**
Triisobutylamine	249	6.28	**4.67**	462	3.50	**1.40**
INORGANIC COMPOUNDS *)						
Sulphurmonoxide	197°	ca. 6.3	**4.2**	411°	3.77	**1.23**
Phosphorustrichloride	183	4.55	**3.41**	349	3.02	**1.17**
Phosphorustribromide	233	3.16	**3.66**	443	3.57	**2.18**
Arsenictrichloride	260	4.19	**2.93**	403.5	3.10	**1.36**
Arsenictribromide	304	3.13	**3.22**	494	2.30	**1.45**

*) Where no special meltingpoint-determinations have been made by us, the best data from literature are used. The little differences of these meltingpointdata are of no importance for the determination of the order of magnitude of K.

INORGANIC COMPOUNDS, (continued).

Chemical Compound:	Absolute Melting-temperature	Specific Cohesion a^2 at the Meltingpoint:	K_m.	Absolute Boiling-temperature: ($p = 1$ atm.)	Specific Cohesion a^2 at the Boilingpoint:	K_b.
Antimonytrichloride	346.2	3.79	**2.46**	496	2.94	**1.29**
Bismuthumtrichloride	506	3.78	**2.35**	—	—	—
Bismuthumtribromide	490	2.96	**2.70**	726	2.28	**1.40**
Stannochloride	523	3.04	**1.10**	876	ca. 4.9	ca. 1.1
Lithiumfluoride	1117	28.4	**0 06**			
Lithiumchloride	887	18.8	**0.89**			
Lithiumsulfate	1122	22.7	**2.22**			
Lithiumnitraat	527	13.5	**1.75**			
Sodiumfluoride	1253	21 14	**0.70**			
Sodiumchloride	1074	14.9	**0.81**			
Sodiumbromide	1034	9.29	**0.92**			
Sodiumiodide	936	6.51	**1.08**			
Sodiumsulphate	1157	19.4	**2.39**			
Sodiummolybdate	960	15.6	**3.34**			
Sodiumwolframate	967	10.66	**3.20**			
Sodiumnitrate	581	12.8	**1.86**			
Sodiummetaphosphate	892	18 8	**1 46**			
Potassiumfluoride	1129	15.2	**0.78**			
Potassiumchloride	1041	13 0	**0.93**			
Potassiumbromide	1006	8.54	**1.01**			
Potassiumiodide	954	6.49	**1.13**			
Potassiumsulphate	1340	15.5	**2.01**			
Potassiumbichromate	669	13.0	**5.71**			
Potassiummolybdate	1192	13.0	**2.60**			
Potassiumwolframate	1194	10.3	**2.81**			
Potassiumnitrate	612	12.4	**2.05**			
Potassiummetaphosphate	1083	20.7	**2.25**			
Rubidiumfluoride	1033	9.24	**1.02**			
Rubidiumchloride	999	9.46	**1.13**			
Rubidiumbromide	956	6.86	**1.19**			
Rubidiumiodide	915	5.83	**1.34**			

INORGANIC COMPOUNDS, (continued).

Chemical Compound:	Absolute Melting-temperature:	Specific Cohesion a^2 at the Meltingpoint:	K_m	Absolute Boiling-temperature: ($p = 1$ atm.)	Specific Cohesion a^2 at the Boilingpoint:	K_b:
	°					
Rubidiumsulphate	1347	10.73	**2.04**			
Rubidiumnitrate	579	8.91	**2.24**			
Caesiumfluoride	953	6.03	**0.96**			
Caesiumchloride	919	6.60	**1.20**			
Caesiumbromide	909	5.42	**1.27**			
Caesiumiodide	894	4.80	**1.39**			
Caesiumsulphate	1292	7.59	**2.13**			
Caesiumnitrate	687	6.78	**1.92**			
Thallonitrate	479	4.89	**2.69**			

means of the so much more extensive experimental material at our disposal now [1]). For the purpose of easier comparison these experimental data are subdivided into four groups · the first group includes all substances, where the mentioned rule, as far as it concerns the *boiling*-temperature, seems to have indeed an approximative validity; it contains **121** compounds. The second group concerns those organic liquids, where the value of K_b is appreciably *smaller*, and **16** liquids are dealt with; while in the third group **14** liquids are collected, for which the mean value is much *greater* than **1,15**. Finally in a fourth group we have dealt with **48** inorganic compounds and metallic salts.

§ **4**. If now we review the results of these calculations, it appears first of all once more, that no complete "law", but only an approximative rule is present here. In the first group the mean value of $\mathbf{K_b}$ is **1,12**, and for $\mathbf{K_m}$ it is **3,38**; thus the mean value at the meltingpoint is *three times* that at the boilingpoint. In 12 or 17 % of the cases considered, dealing with **121** substances for the boilingpoints, and **118** for the meltingpoints, there are rather appreciable deviations from this mean value stated: at the boiling-

[1]) The number for a^2 therein is calculated from: $\frac{2\chi}{gd}$ at the melting, or boilingpoint

point the greatest differences can reach 16 %, at the meltingpoints in some cases even 58 % of this mean value. In every case the rule holds at the boilingpoint evidently much better than at the meltingpoint, — which could be expected beforehand. In group II we find: *water*, the *alcools*, the *acids*, and a number of aliphatic *amines*, — all substances for which association is also very probable as concluded from other phenomena. In group III we find i.a. the neutral *glycerides* of the fatty acids; it is very difficult to give a sufficient explanation for the very high values K_b in these cases, but it seems that the extremely great molecular weights of these compounds play a certain role in the results of the calculations. Abnormally small however, and without any regularity, are the values for K_m in the case of the molten inorganic salts; in this respect it is worth attention, that in the series of the alcali-halogenides, K_m seems to increase in general with increasing atomic weight of the halogen. These inorganic salts are thus evidently to be grouped apart, and they are certainly deviating further from the organic liquids, than e.g. such is the case with the halogenides of *P* and *As*.

	Li	*Na*	*K*	*Rb*	*Cs*
F	0.66	0.70	0.78	1.02	0.96
Cl	0 89	0.81	0.93	1.13	1.20
Br	—	0.92	1.01	1.19	1.27
I	—	1.08	1.13	1.34	1.39

Generally speaking, we can thus say that in by far the greatest number of organic compounds, the empirical rules of WALDEN are *confirmed* by experiment, and that the mean value at the meltingpoint is very closely *three* times that at the boilingpoint. However it may appear doubtful, if it is right to conclude about the *degree* of association of these liquids, from the deviations, which are observed with respect to the adopted mean values.

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