390. *The Thermodynamic Functions of the Vinyl Halides.*

By R. E. Richards.

The thermodynamic functions, namely, entropy, free-energy function, heat-content function, and heat capacity, have been calculated for the vapours of vinyl chloride, bromide, and iodide, over the temperature range 291—1500° K.

Since there appear to be no accurate measurements of the thermodynamic functions of the vinyl halides in the literature, and in view of the importance of these substances, it was thought that the calculation of these quantities might be useful. The calculations have been made for vinyl chloride, bromide, and iodide over a wide range of temperatures. Similar calculations for vinyl chloride have been carried out by Godnev and Filatova [*Compt. rend.* (*Doklady*) *Acad. Sci. U.R.S.S.*, 1946, **52**, 43] at a few temperatures.

The following calculations have been made using the fundamental constants given by Birge (*Rev. Mod. Physics*, 1941, **13**, 233; *J.*, 1946, 219). The translational–rotational entropy at one atmosphere is then given by the equation :

$$S°_{t.r.} = 2{\cdot}2870\ (8 \log T + 3 \log M + \log ABC - 2 \log \sigma) - 9{\cdot}2069 \text{ e.u.}$$

The logarithms are to the base 10, T is the absolute temperature, M is the molecular weight, A, B, and C are the principal moments of inertia of the molecule in units $\times 10^{-40}$ g.-cm.^{2}, and σ is the symmetry number. The values of the entropy are, of course, the "virtual entropy" and do not include nuclear-spin contributions. The molecular dimensions and frequencies used and the results of the calculations are tabulated below. The moments of inertia were calculated by the method of Hirschfelder (*J. Chem. Physics*, 1940, **8**, 431) and inserted into the expression for $S°_{t.r.}$ together with the symmetry number, $\sigma = 1$, to give the results of the last three tables. In order to find the error introduced by the uncertainty in the molecular dimensions, the products of the moments of inertia were calculated for the most different possible dimensions, and the new values of $S°_{t.r.}$ computed. Errors in $S°_{t.r.}$ of the order of 0·1 e.u. can be obtained, so that, although the values for the entropies have been given to the second decimal place, it must be remembered that this could be subject to a maximum possible error of the order of 0·1 e.u. In the last three tables the various units are cals., °c., moles, except for $(H° - E°_0)$ which is in kcal./mole.

The vibrational contributions to these quantities are summed with the aid of the tables compiled by E. B. Wilson, junr., and corrected to the basis of new constants (see Taylor and Glasstone, "A Treatise on Physical Chemistry," Vol. 1), the vibrations being assumed harmonic. The errors involved in this assumption and in neglecting the existence of isotopic molecules are certainly not greater than other inaccuracies involved.

Molecular dimensions used.

	Bond lengths, A.*			$I \times 10^{40}$, g.-cm.^{2}.			
Compound.	C–H.	C=C.	C–Hal.	*A*.	*B*.	*C*.	ν, cm.$^{-1}$.†
C_2H_3Cl	1·08	1·38	1·69 ± 0·02	15·7	135·7	151·4	395, 622, 724, 895, 940, 1030, 1280, 1370, 1610, 3030, 3080, 3130
C_2H_3Br	1·08	1·34	1·86 ± 0·04	16·0	195·0	210	345, 497, 615, 902, 940, 1008, 1262, 1377, 1605, 3014, 3076, 3100
C_2H_3I	1·09	1·34	2·03 ± 0·04	17	240	257	309, 435, 535, 909, 946, 990, 1229, 1376, 1593, 3000, 3060, 3110

* C_2H_3Cl : Brockway, *J. Chem. Physics*, 1936, **8**, 231. C_2H_3Br and C_2H_3I : Hugill, Coop, and Sutton, *Trans. Faraday Soc.*, 1938, **34**, 1518. All angles are assumed to be 120°, except in vinyl iodide for which the HCH angle is 120° and the HCI angle is 122°.

† C_2H_3Cl and C_2H_3Br : Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 21. C_2H_3I : *idem*, *J.*, 1944, 303.

Temp.,	Entropy.			$-(G° - E°_0)/T$.		$\frac{(H° - E°_0)}{T}$,	$(H° - E°_0)$,		
° K.	$S°_{t.r.}$.	$S_{vib.}$.	$S°_{total}$.	Vib.	Total.	Vib.	Total.	$C_{vib.}$.	$C°_p$.
				Vinyl chloride.					
291·16	60·80	1·961	62·76	0·516	53·36	1·444	2·734	4·676	12·622
298·16	60·98	2·076	63·06	0·552	53·59	1·524	2·824	4·879	12·824
300	61·03	2·111	63·14	0·563	53·64	1·548	2·848	4·936	12·882
350	62·26	2·972	65·23	0·843	55·16	2·128	3·526	6·314	14·260
400	63·32	3·903	67·22	1·167	56·54	2·736	4·273	7·611	15·557
450	64·25	4·867	69·12	1·524	57·83	3·343	5·080	8·773	16·719
500	65·09	5·848	70·94	1·907	59·05	3·940	5·943	9·841	17·787
550	65·85	6·831	72·68	2·311	60·21	4·520	6·856	10·791	18·737
600	66·54	7·810	74·35	2·728	61·32	5·082	7·817	11·658	19·604
650	67·18	8·770	75·95	3·155	62·39	5·615	8·815	12·432	20·378
700	67·77	9·719	77·48	3·591	63·41	6·128	9·852	13·143	21·089
750	68·31	10·649	78·96	4·031	64·40	6·619	10·923	13·797	21·743
800	68·83	11·560	80·39	4·473	65·35	7·087	12·026	14·401	22·347
850	69·31	12·445	81·75	4·914	66·28	7·532	13·156	14·955	22·901
900	69·76	13·321	83·08	5·360	67·18	7·961	14·316	15·542	23·488
1000	70·60	15·003	85·60	6·244	68·90	8·758	16·704	16·398	24·344
1200	72·04	18·129	90·18	7·966	72·07	10·164	21·731	17·897	25·843
1500	73·82	22·302	96·12	10·422	76·30	11·879	29·738	19·491	27·437

Temp., ° K.	Entropy. $S°_{t.r.}$.	$S_{vib.}$.	$S°_{total}$.	$-(G° - E°_0)/T$. Vib.	Total.	$\frac{(H° - E°_0)}{T}$, Vib.	$(H° - E°_0)$, Total.	$C_{vib.}$.	$C°_p$.
				Vinyl bromide.					
291·16	63·11	2·560	65·67	0·738	55·90	1·823	2·844	5·301	13·247
298·16	63·29	2·689	65·98	0·782	56·13	1·907	2·938	5·492	13·437
300	63·34	2·723	66·06	0·794	56·19	1·929	2·962	5·541	13·487
350	64·57	3·677	68·24	1·137	57·76	2·540	3·670	6·862	14·808
400	65·63	4·675	70·30	1·516	59·20	3·159	4·442	8·087	16·033
450	66·56	5·693	72·26	1·923	60·54	3·769	5·272	9·204	17·150
500	67·40	6·715	74·12	2·351	61·81	4·364	6·155	10·211	18·157
550	68·16	7·732	75·89	2·795	63·01	4·937	7·085	11·119	19·065
600	68·85	8·736	77·58	3·248	64·15	5·488	8·060	11·942	19·888
650	69·49	9·720	79·21	3·707	65·25	6·013	9·073	12·691	20·637
700	70·07	10·685	80·76	4·171	66·30	6·514	10·122	13·376	21·322
750	70·62	11·631	82·25	4·637	67·32	6·994	11·205	14·008	21·954
800	71·14	12·556	83·69	5·105	68·29	7·451	12·318	14·592	22·538
850	71·62	13·453	85·07	5·567	69·24	7·886	13·457	15·133	23·079
900	72·07	14·341	86·41	6·035	70·16	8·306	14·626	15·636	23·582
950	72·50	15·199	87·70	6·495	71·05	8·705	15·818	16·105	24·051
1000	72·91	16·031	88·94	6·948	71·91	9·084	17·029	16·538	24·484
1200	74·36	19·183	93·54	8·728	75·14	10·455	22·081	18·007	25·953
1500	76·13	23·379	99·51	11·247	79·43	12·132	30·117	19·573	27·518
				Vinyl iodide.					
291·16	64·65	3·063	67·71	0·943	57·65	2·120	2·931	5·714	13·659
298·16	64·84	3·202	68·04	0·995	57·89	2·207	3·027	5·896	13·842
300	64·89	3·237	68·13	1·009	57·95	2·229	3·052	5·944	13·890
350	66·11	4·250	70·36	1·398	59·57	2·852	3·779	7·218	15·164
400	67·17	5·295	72·47	1·821	61·05	3·474	4·568	8·401	16·347
450	68·11	6·343	74·45	2·263	62·43	4·080	5·412	9·479	17·424
500	68·95	7·392	76·34	2·724	63·72	4·668	6·307	10·450	18·396
550	69·74	8·433	78·17	3·196	64·99	5·237	7·251	11·338	19·284
600	70·40	9·454	79·85	3·676	66·13	5·779	8·235	12·138	20·084
650	71·03	10·459	81·49	4·161	67·25	6·298	9·258	12·868	20·814
700	71·62	11·439	83·06	4·647	68·32	6·792	10·317	13·537	21·483
750	72·17	12·390	84·56	5·129	69·35	7·261	11·406	14·154	22·099
800	72·68	13·324	86·01	5·613	70·35	7·711	12·525	14·726	22·672
850	73·16	14·299	87·39	6·091	71·31	8·138	13·672	15·255	23·201
900	73·62	15·122	88·74	6·572	72·24	8·550	14·846	15·750	23·696
950	74·05	15·982	90·03	7·043	73·14	8·940	16·041	16·207	24·153
1000	74·45	16·825	91·28	7·512	74·02	9·314	17·259	16·636	24·582
1200	75·90	19·994	95·90	9·333	77·29	10·661	22·328	18·080	26·026
1500	77·68	24·201	101·88	11·892	81·62	12·309	30·382	19·625	27·571

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