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Thermodynamic Properties of Galvinoxyl Radical and Its Phenol Derivative; Mechanism of the Phase Transition*1

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Measurements of heat capacity of Galvinoxyl radical and its phenol derivative were carried out in the temperature region from 12 to 300°K. Galvinoxyl radical exhibits a phase transition of first-order nature at 81.5°K which corresponds to the susceptibility anomaly already measured. The enthalpy and entropy of transition amount to 1504.6 J/mol and 18.67 J/(°K·mol), respectively. The entropy change, which corresponds formally to $\boldsymbol{R} \ln 9.45$, cannot be explained by taking only the magnetic contribution. On the other hand, its phenol derivative, the corresponding diamagnetic substance, has not thermal anomaly in the above temperature region. X-Ray diffraction patterns at room temperature for both substances agree well with each other in their diffraction angles. From these experimental findings, it seems to be plausible that a kind of transformation of the crystal structure of Galvinoxyl radical takes place at the transition point which may be induced by a pairing of magnetic spins between neighboring molecules.

Recently, magnetic properties of stable organic free radical crystals have attracted interest of many chemists and physicists. Among these crystals, tetracyano-quinondimethane (TCNQ salts) as anion radicals, Würster Blue (WB salts) as cation radicals and 1,3-bisdiphenylene-2-phenyl allyl (BDPA) as a neutral one would be the typical substances. As the molecular structures of these radicals are considered to be planar, the magnetic properties of crystals composed of these molecules would be similar to each other.

The present substance, Galvinoxyl radical, 2,6-di-*t*-butyl-4(3,5-di-*t*-butyl-4-oxocyclohexa-2,5-dienylidene methyl) phenoxyl (hereafter, designated as G. R., see Fig. 1) is considered to be composed of non-planar molecules due to the mutual intramolecular steric hindrance of the attached tertial butyl groups. Accordingly, it is expected that the physico-chemical properties of G. R. may be different more or less from those of the radical crystals mentioned above. The magnetic susceptibility of G. R.1) has already been measured by two of the present authors (K. M. & Y. D.) and H. Nishiguchi. According to their results, G. R. is paramagnetic above the magnetic transition point, 82.5°K, where the susceptibility drops down very sharply on cooling. We have undertaken the measurement of heat capacity from 13 to 300°K through the transition point in order to study the mechanism of this magnetic anomaly. Furthermore, we have measured the heat capacity of its phenol derivative, 2,6-di-*t*-butyl-4 (3,5-di-*t*-butyl-4-oxocyclohexa-2,5-dienylidene methyl) phenol (see Fig. 1) for comparison, in order to elucidate the effect of the radical nature on the properties of G. R.

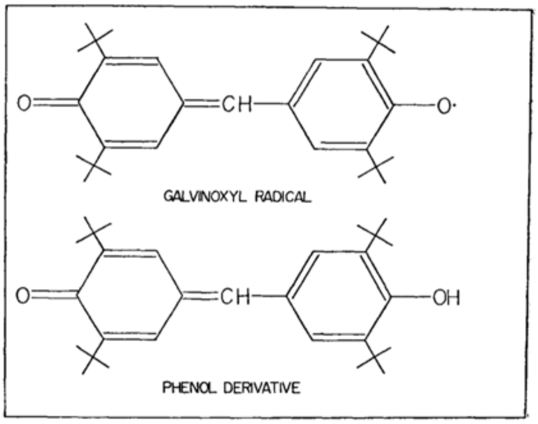

Fig. 1. Molecular Structures of galvinoxyl radical and its phenol derivative.

+: Tertial butyl group

Experimental

Samples. G. R.2) was synthesized from 2,6-di-*t*-butyl phenol. After condensation with formaldehyde

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1) K. Mukai, H. Nishiguchi and Y. Deguchi, *J. Phys. Soc. Japan*, **23**, 125 (1967).

2) M. S. Kharasch and B. S. Joshi, *J. Am. Chem. Soc.*, **79**, 1439 (1957).

the product was oxidized by lead dioxide. Needle crystals of blue-black color were obtained.

Yellow needle crystal of its phenol derivative were prepared by the reaction between G. R. and di(3,5-di-*t*-butyl-4 hydroxy phenyl) methane in ether solution.

The both substances were ground, in a dry box to the fine powders for packing it into a calorimeter cell. The weight of G. R. used for measurement was 13.6159 g. The radical concentration was determined to be 106± 5% from the value of the Curie constant derived from the data of susceptibility above 82.5°K. The weight of the phenol derivative used for measurement was 18.6619 g.

Calorimeter and Cryostat. Adiabatic type calorimeter and cryostat[3] described previously were used for measurement of the heat capacity. Gold cell, provided with a platinum resistance thermometer, heater and inner platinum fins for thermal conduction, was used in order to avoid the chemical reaction with the radical. Measurements of heat capacities were performed from 11 to 300°K.

X-Ray Analysis. Taking the Debye-photographs of the samples, the identification was made at room temperature.

Results

Experimental data are listed for G. R. in Table 1 and for its phenol derivative in Table 2. These data are based on a molecular weight of 421.649 g for G. R. and 422.657 g for its phenol derivative and also on the relation 0°C=273.15°K. The heat capacities in these tables are the ratio of the increase in enthalpy to the rise in temperature and are equal to the differential heat capacity only when the correction for curvature is negligible. The temperature T listed in these tables is the arithmetic mean of the initial and the final temperature.

As are shown the experimental data of G. R.

TABLE 1. HEAT CAPACITIES OF GALVINOXYL RADICAL

T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT	T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT	T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT
12.702	17.458	2.7800	78.259	230.68	.93011	149.494	349.42	4.0629
15.035	23.795	1.8858	79.186	254.15	.92372	153.529	358.03	4.0071
17.055	28.495	2.1549	80.089	303.88	.88380	157.512	365.63	3.9590
19.014	34.567	1.7627	80.296	370.22	2.4249	161.456	373.79	3.9285
21.079	40.109	2.3677	80.877	502.94	.69032	165.353	381.19	3.8687
23.277	46.616	2.0273	81.479	816.74	.51397	168.934	389.13	3.8320
25.505	52.665	2.4695	82.170	310.85	.86849	172.898	396.91	4.0954
28.063	60.008	2.6055	83.110	204.30	1.0121	177.249	405.65	4.6070
30.779	66.981	2.8270	84.636	204.73	2.1154	181.830	414.58	4.5549
33.443	74.917	2.5021	85.161	206.10	.99793	186.359	423.22	4.5028
36.050	81.811	2.7116	86.157	206.48	.99259	190.837	432.17	4.4536
38.651	87.800	2.4894	86.736	208.97	2.0833	195.266	441.73	4.4045
40.981	92.988	2.1708	87.147	208.53	.98680	199.650	449.45	4.3626
43.336	99.225	2.5394	88.143	209.70	1.0055	203.989	458.19	4.3165
46.028	104.43	2.8443	88.804	213.49	2.0537	208.286	466.21	4.2766
48.784	111.12	2.6689	89.135	212.39	.97842	212.541	474.66	4.2336
51.383	117.26	2.5277	90.108	216.47	.96735	216.755	482.41	4.1958
53.652	122.19	2.0112	90.843	217.67	2.0260	220.931	490.19	4.1569
56.458	129.00	3.6005	91.439	218.13	1.6940	225.070	498.08	4.1206
59.540	137.72	2.5641	93.126	221.68	1.6795	229.179	507.02	4.0969
62.056	145.52	2.4670	94.797	225.23	1.6629	233.249	514.92	4.0437
64.479	153.76	2.3794	96.490	230.32	3.6126	237.940	524.23	5.3373
66.823	159.78	2.3092	100.443	240.40	4.2938	242.868	534.57	5.3131
67.508	162.59	3.5903	104.806	250.40	4.4319	248.144	547.51	5.2444
69.097	167.18	2.2415	109.613	261.24	5.1823	253.357	558.59	5.1869
71.054	172.97	3.4842	114.620	272.30	4.8319	258.516	569.54	5.1306
71.401	174.12	2.3713	119.398	283.37	4.7248	263.620	579.59	5.0785
73.397	183.10	1.6205	123.995	293.65	4.4685	268.742	591.97	5.1618
74.415	188.50	3.2612	128.442	303.18	4.3857	274.136	603.79	5.6259
75.564	196.47	.89499	132.770	312.91	4.3102	280.470	617.18	7.0406
76.451	202.42	.87981	137.045	322.33	4.2401	287.471	631.52	6.9642
77.343	212.49	.90234	141.253	331.52	4.1766	294.145	643.55	6.3863
77.567	219.90	3.0428	145.402	340.11	4.1207	300.481	659.42	6.2880

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[3] T. Matsuo, H. Suga and S. Seki, Preprint of the 3rd Japanese Calorimetry Conference, B104, 40 (1967).

TABLE 2. HEAT CAPACITIES OF THE PHENOL DERIVATIVE

T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT	T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT	T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT
12.341	16.392	2.5211	77.369	185.43	2.3275	165.554	387.15	5.0547
14.472	22.616	1.7402	79.654	191.06	2.2964	170.568	397.59	4.9738
16.069	27.313	1.4538	81.530	196.01	1.4460	175.505	407.55	4.9015
17.410	31.810	1.2280	82.897	199.18	1.2792	180.368	417.42	4.8278
17.538	32.285	3.1236	84.169	202.89	1.2642	185.162	426.94	4.7607
20.055	39.851	1.8192	85.426	205.80	1.2508	189.892	436.68	4.6959
21.747	44.891	1.5660	86.671	208.98	1.2378	194.871	446.34	5.2555
23.951	51.576	2.8426	87.902	212.36	1.2244	200.099	456.72	5.1906
26.522	59.324	2.3992	89.121	214.89	1.2140	205.255	467.11	5.1192
29.044	65.626	2.5446	90.330	217.61	1.2033	210.399	477.14	5.0515
31.586	72.920	2.5390	91.528	220.20	1.1936	215.359	486.95	4.9870
34.196	80.460	2.6808	92.716	223.77	1.1820	220.314	497.43	4.9175
36.872	87.206	2.6711	93.893	225.57	1.1739	225.203	506.49	4.8606
39.436	93.290	2.4568	95.062	228.61	1.1614	229.942	516.66	4.7989
41.709	98.817	2.0904	96.666	232.63	2.0434	234.804	525.92	4.7442
44.062	104.82	2.6150	99.030	238.41	2.6839	239.521	535.05	4.6902
46.597	110.36	2.4533	101.691	245.03	2.6376	244.351	544.33	4.9699
49.101	116.72	2.5518	104.966	252.82	3.9141	249.286	554.30	4.9048
51.715	124.29	2.6780	109.464	264.74	5.1053	254.186	564.32	4.8934
53.915	127.85	1.7229	114.508	274.24	4.9829	259.021	573.52	4.7972
56.022	132.53	2.4912	119.425	286.62	4.8522	263.800	583.64	4.7421
58.464	138.40	2.3933	124.223	297.64	4.7426	268.516	593.38	4.6897
60.922	144.95	2.5218	129.050	308.60	4.9107	273.949	604.43	6.1758
63.385	151.81	2.4614	133.908	319.48	4.8069	280.592	617.01	6.2484
65.806	157.89	2.3808	139.093	331.14	5.5653	286.262	629.05	6.1654
68.139	163.63	2.2909	144.598	343.86	5.4435	292.371	642.30	6.0724
70.402	168.56	2.2343	149.986	355.35	5.3329	298.454	652.49	6.0926
72.712	174.24	2.3859	155.269	366.19	5.2342			
75.069	179.95	2.3275	160.456	377.06	5.1399			

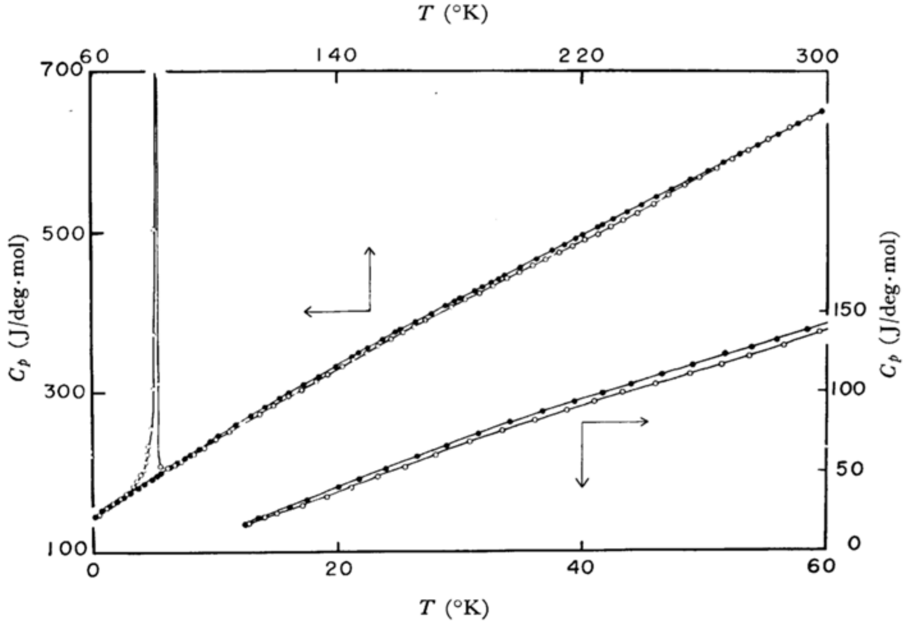

Fig. 2. Heat capacity of galvinoxyl radical and its phenol derivative.
Galvinoxyl radical: ○ Its phenol derivative: ●

TABLE 3. SMOOTHED VALUES OF HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF GALVINOXYL RADICAL

T (°K)	$C_p°$ (J/°K·mol)	$S°$ (J/°K·mol)	$(H°-H_0°)/T$ (J/°K·mol)	$-(G°-H_0°)/T$ (J/°K·mol)
15	23.60	9.543	7.040	2.503
20	37.20	18.182	12.868	5.314
30	65.68	27.927	25.666	12.907
40	91.20	61.042	38.928	22.114
50	113.65	83.839	51.656	32.183
60	139.19	106.70	64.006	42.691
70	170.59	130.54	77.003	53.351
80	292.18	157.18	92.589	64.594
90	215.03	196.32	118.67	77.646
100	239.16	220.18	129.47	90.706
120	284.91	267.82	151.55	116.26
140	328.68	315.09	173.81	141.28
160	370.57	361.78	195.89	165.93
180	411.00	407.75	217.50	190.25
200	450.18	453.08	238.80	214.27
220	488.53	497.82	259.81	238.02
240	529.46	542.07	280.55	261.52
260	572.88	586.16	301.37	284.79
280	616.15	630.20	322.31	307.89
300	658.28	671.96	343.30	328.66

TABLE 4. SMOOTHED VALUES OF HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF ITS PHENOL DERIVATIVE

T (°K)	$C_p°$ (J/°K·mol)	$S°$ (J/°K·mol)	$(H°-H_0°)/T$ (J/°K·mol)	$-(G°-H_0°)/T$ (J/°K·mol)
15	25.31	9.717	7.203	2.514
20	40.00	19.054	13.604	5.450
30	68.71	40.685	27.103	13.582
40	94.80	64.151	40.874	23.277
50	118.84	87.901	54.075	33.826
60	142.56	111.51	66.779	44.731
70	167.67	135.43	79.456	55.973
80	192.04	159.39	91.992	67.402
90	216.88	183.47	104.51	78.958
100	240.91	207.54	116.93	90.613
120	287.93	255.68	141.56	114.11
140	333.29	303.48	165.72	137.76
160	376.08	350.84	189.40	161.44
180	416.85	397.49	212.41	185.09
200	456.49	443.45	234.83	208.63
220	496.02	488.81	256.79	232.03
240	536.17	533.70	278.40	255.30
260	575.46	578.17	299.74	278.43
280	616.40	622.34	320.92	301.42
300	658.35	666.29	342.01	324.29

TABLE 5. THERMODYNAMIC FUNCTIONS OF GALVINOXYL RADICAL (I) AND ITS PHENOL DERIVATIVE (II) AT 298.15°K

Unit; (J/°K·mol)

	$C_p°$	$S°$	$(H°-H_0°)/T$	$-(G°-H_0°)/T$
I	654.28	670.10	341.36	328.74
II	654.28	662.24	340.06	322.18
I−II	000.00	7.86	1.30	6.56

Table 6. Anomalous heat capacity of galvinoxyl radical

T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT	T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT	T (°K)	$\Delta H/\Delta T$ (J/°K·mol)	ΔT
62.056	0.585	2.4670	74.415	11.675	3.2612	80.877	309.95	0.69032
64.479	2.233	2.3794	75.564	16.580	0.89499	81.479	622.17	0.51379
66.823	3.355	2.3092	76.451	20.331	0.87981	82.170	114.42	0.86846
67.508	4.246	3.5903	77.343	28.293	0.90234	83.110	5.794	1.0121
69.097	5.004	2.2415	79.186	64.286	0.92372	84.636	2.570	2.1154
71.045	5.710	3.4842	78.259	44.378	0.93011	85.161	2.635	0.99793
71.401	5.740	2.3713	80.089	112.77	0.88380	86.736	1.651	2.0833
73.397	8.998	1.6205	80.296	178.58	2.4249			

with the open circles in Fig. 2, an exceedingly sharp anomaly is found at 81.5°K. Around the transition temperature, it takes a long time (1—2 hr) for thermal equilibration, so that the heat capacity values in these regions are inferior in accuracy to those in the normal region where the thermal relaxation time is of the order of 2—4 min. The heat capacity peak is so sharp that 90% of the whole enthalpy change occurs in the narrow range of 3°K. Although the latent heat effect could not be observed exactly on account of the experimental difficulty, it is highly probable that the transition is of the first order. Three independent runs were performed for the determination of the enthalpy change of the transition. The average value is found to be 1504.56±5.34 J/mol. The entropy of the transition is 18.674 J/(°K·mol). This value corresponds formally to $\boldsymbol{R}\ln 9.45$. The anomalous heat capacity has a tail extending down to about 60°K and sharply decreases to the normal value at the higher temperature side.

Experimental data of its phenol derivative are plotted with the filled circles in Fig. 2 with those of G. R. The result stands in contrast with that of G. R. in the point that no thermal anomaly is observed at the temperature region of G. R. Smoothed values of the heat capacity, enthalpy, entropy and Gibbs-energy functions are listed for G. R. in Table 3 and of its phenol derivative in Table 4. Values of their thermodynamic functions at 298.15 K are listed in Table 5. The detailed values of the anomalous heat capacity are listed in Table 6.

Discussions

In the present time we know only three free radical crystal whose heat capacity had been measured. Among them, for BDPA[4] and tetramethyl-2,2,6,6-piperidol-4-oxyl-1,[5] their heat capacity data show that there is no phase transition and their behaviors of the magnetic heat capacity are explained with a linear Ising and Heisenberg models with a coupling between neighboring chains. On the other hand, the heat capcacity data of Wüster Blue Perchlorate (WBP)[6] shows that there is a phase transition at 189.9 K which is corresponding to the magnetic transition temperature.[7,8] The mechanism of this magnetic transition has been discussed by Chesnut[9] and McConnell[10,11] and others. Chesnut explained the mechanism by the model of exciton-exciton interactions. McConnell *et al.* on the other hand, investigated the pressure dependence of the magnetic transition of WBP and $(C_6H_5)_3PCH_3(TCNQ)_2$ and found that this magnetic transition took place even under the low exciton density. Based on these observation, it seems to be improbable that the exciton-exciton interactions make the transition to be cooperative. Moreover the change of crystal structure of WBP[12] was observed by the X-ray analysis. According to these facts, it may be plausible to consider that the magnetic anomaly is induced by the change of the crystal structure.[13]

Now, turning to the present substances investigated, the measurement of the magnetic susceptibility of G. R.[1] shows the magnetic transition at 82.5°K and G. R. was found to be paramagnetic above the transition temperature and to be diamagnetic (weak paramgnetic[14]) below it. The sharp rise of the magnetic susceptibility from the low temperature side of the transition is considerablly

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4) A. S. Edelstain and M. Mandel, *J. Chem. Phys.*, **35**, 1130 (1961); W. O. Hamilton and G. E. Pake, *ibid.*, **39**, 2694 (1963).

5) H. Lemaire, P. Rey, A. Rassat, A. D. Combarieu and J. C. Michel, *Mol. Phys.*, **14**, 207 (1968).

6) H. Chihara, M. Nakamura and S. Seki, This Bulletin, **38**, 1776 (1965).

7) K. Okumura, *J. Phys. Soc. Japan*, **18**, 69 (1963).

8) W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

9) D. B. Chesnut, *ibid.*, **40**, 405 (1964).

10) A. W. Merkel, R. C. Hughes, L. J. Berliner and H. M. McConnell, *ibid.*, **43**, 953 (1965).

11) R. C. Hughes, A. W. Merkel and H. M. McConnell, *ibid.*, **44**, 1720 (1966).

12) D. D. Thomas, H. Keller and H. M. McConnell, *ibid.*, **39**, 2321 (1963).

13) G. T. Pott and J. Kommandour, *ibid.*, **47**, 395 (1967); H. J. Monkrost, G. T. Pott and J. Kommandour, *ibid.*, **47**, 401 (1967); G. T. Pott, C. F. van Bruggen and J. Kommandour, *ibid.*, **47**, 408 (1967).

14) K. Mukai, This Bulletin, **42** (1969), in press.

different from those of BDPA and WBP. This behavior cannot be explained only by use of a model of magnetic chains linearly interacted, but may be interpreted in such a way that a kind of pairing process of spins is assumed with, large J-value below the transition temperature and small J-value above it. If this kind of pairing state be of singlet (dimerization of spins), entropy change for this process amounts to $\boldsymbol{R} \ln 2$. The present results of the heat capacity, however, revealed that the entropy change associated with the phase transition is found to be $\boldsymbol{R} \ln 9.45$. There is a large difference, $\boldsymbol{R} \ln 4.73$ between them. In order to explain this large discrepancy, we may expect that the magnetic pairing process may be accompanied with a cooperative change of crystal structure. In this respect, it is very much desirable to study the crystal structure of the low temperature phase of this material.

We may proceed to the case of the diamagnetic phenol derivative. As is shown in Fig. 2 in the temperature above the transition points of G. R., the heat capacities of the phenol derivative are at the most 2% larger than those of G. R. While below the transition region the heat capacities of the phenol are about 5% larger than those of G. R. These facts probably mean that the crystal structure of G. R. changes at the transition temperature, whereas that of the phenol derivative does not. The results of measurements of the heat capacity and of X-ray analysis show that the crystal structure of G. R. is almost the same to that of the phenol derivative at room temperature. Therefore, we should like to consider that the phase transition of G. R. is induced by a cooperative process of pairing of magnetic spins in contrast to the case of WBP. In conection with this point of view, it may be recalled that some authors[13] attributed the phase transition of WBP to the order-disorder transition of perchlorate ion accompanied with the charge-transfer of TMPD cores. In this case perchlorate ions are in an ordered state with respect to their orientation below its transition temperature. This process results in the difference of the electrostatic potential at TMPD cores and therefore is accompanied by the charge-transfer. Here, the unpaired electrons are localized in one of the two molecules in this model. However it may be, this charge-transfer state may be called rather ionic-bonded one. On the analogy of this process, one may propose that the magnetic transition of G. R. is induced by the creation of "covalent-like" bond between two molecules. For, in contrast to the existence of perchlorate ion between WB ions, molecules of G. R. are directly in contact with each other. From this points of view, the symbol J given above means the coulomb integral rather than the exchange one.

Apart from the discussion of the phase transition of the stable free radical crystal, we may illustrate the following facts for reference.

There are known some substances which change their crystal structures accompanied with magnetic anomaly. Vanadium dioxide is one of the case. The crystal structure of the low temperature phase of this compound constitutes a deformed lattice of the rutile-type structure and that of the high temperature phase constitutes the normal rutile-type one.[15] This substance has a magnetic anomaly[16] at the corresponding transition temperature. Some authors[17] assume the appearance of metal-metal bond in its crystal, since the metal-metal distance is found to be shortened at the lower temperature phase. Our model adopted to explain the mechanism of the phase transition of G. R. may be looked upon as a similar kind one.

Summary

The heat capacities of G. R. and its phenol derivative were measured in order to study the nature of the magnetic anomaly. It was found that the heat capacity of G. R. shows an anomaly at 81.5°K which just corresponds to the magnetic transition temperature. The enthalpy and entropy of transition are 1504.6 J/mol and 18.67 J/(°K·mol) (*i. e.* $\boldsymbol{R} \ln 9.45$). The heat capacity of its phenol derivative, on the other hand, has no anomaly at the temperature region measured. The thermodynamic functions for both substances were evaluated by integrating respective heat capacity data. The values at 298.15°K are, in units of J/(°K·mol); $C_p{}^\circ = 654.28$, $S^\circ = 670.10$, $(H^\circ - H_0{}^\circ)/T = 341.31$, $-(G^\circ - H_0{}^\circ)/T = 328.74$ for Galvinoxyl radical, $C_p{}^\circ = 654.28$, $S^\circ = 662.24$, $(H^\circ - H_0{}^\circ)/T = 340.04$, $-(G^\circ - H_0{}^\circ)/T = 322.18$ for its phenol derivative.

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15) S. Westman, *Acta Chem. Scand.*, **15**, 217 (1961).

16) W. Klemm and E. Hoschek, *Z. anorg. allgem. Chem.*, **226**, 359 (1936).

17) B. O. Marinder and A. Mangell, *Acta Chem. Scand.*, **11**, 1635 (1957); T. Kawakubo and T. Nagasaki, *J. Phys. Soc. Japan*, **19**, 517 (1964).