Thermodynamic Properties and Phase Transitions of Methyltriphenylphosphonium and Methyltriphenylarsonium Bis(7,7,8,8-tetracyanoquinodimethanide)s and Their Solid Solutions*

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The heat capacities of stable organic free-radical salts $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3AsCH_3]_x{}^+(TCNQ)_2{}^{\overline{\cdot}}$ (x=0, 0.159, 0.250, 0.449, and 1, and TCNQ=7,7,8,8-tetracyanoquinodimethane) have been measured with an adiabatic calorimeter in the temperature range between 12 and 370 K. The phase transitions are found for the former four cases at 315.65, 325.80, 333.05, and 357.92 K, respectively. The enthalpy and the entropy due to the phase transitions are determined. The transition temperature is raised by diluting the phosphonium salt with the arsonium one. This tendency is quite contrary to that found for usual solid solutions. The magnitude and the composition dependence of the transition entropy indicate that the phase transition of the solid solutions may be attributable to the changes in both the crystal structure and the magnetic spin state at the transition point. A plausible explanation for the present unusual tendency for the composition dependence is presented.

Organic anion radical salts based on 7,7,8,8-tetracyanoquinodimethane(TCNQ) have been found to exhibit very high electric conductivity and unusual magnetic properties.[1] The unpaired electron of a TCNQ anion radical is not necessarily lacalized on a particular atom but distributed over a whole TCNQ radical to a considerable extent.[2] The rather easy flip-flop motion of the unpaired electrons between adjacent radicals forming a column in a crystal brings about high electric conductivity. Because of the unique interaction of the spins associated with the unpaired electrons, the ground spin manifold is not a doublet but a singlet with a thermally accessible triplet state. Owing to these situations neither the localized spin model nor the continuous band model due to the collective motion of conduction electrons can describe satisfactorily the magnetic properties of anion radical salts. These peculiar behavior is of course expected to be reflected on their thermal properties.

In a previous publication[3] we reported briefly the heat capacity of methyltriphenylphosphonium bis(7,7,8,8-tetracyanoquinodimethanide)[abbreviated hereafter as $[(C_6H_5)_3PCH_3]^+(TCNQ)_2{}^{\overline{\cdot}}$ or more simply as the P-salt] and pointed out that the phase transition observed at T_c=315.65 K cannot be described solely by the spin contribution. Based on the analysis of the transition entropy, it was predicted that the phase transition may be accompanied by a crystallographic change. The precise structural analyses by X-ray diffraction[4,5] demonstrated really the existence of a structural change at T_c. In the present paper we report thermodynamic properties and phase transitions of the P-salt and the methyltriphenylarsonium homolog[abbreviated as $[(C_6H_5)_3AsCH_3]^+(TCNQ)_2{}^{\overline{\cdot}}$ or more simply as the As-salt] as well as their solid solutions $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3AsCH_3]_x{}^+(TCNQ)_2{}^{\overline{\cdot}}$($x$=0.159, 0.250 and 0.449).

Since the first synthesis of these radical salts,[6] extensive studies have been made by means of electron paramagnetic resonance (EPR),[7–13] electric conductivity,[14–18] magnetic susceptibility[19] and of high-pressure experiment[20,21] and also by theoretical treatment.[22–25] As to the mechanism of phase transition, two simple phenomenological models have been reported.[20,23] On the one hand, Chesnut[23] tried to interpret the transition mechanism of the P-salt by assuming that the spin state exists in a singlet-triplet equilibrium with the attractive interaction between triplets. His model accounts for the occurrence of phase transition when adequate values be assigned to the triplet excitation energy and to the exciton-exciton interaction energy. On the other hand, Merkl *et al.*[20] observed the pressure-induced phase transition for the P- and the As-salts and explained the p-T phase diagram for the As-salt in terms of an elementary theory of non-interacting triplet excitons. These two models succeeded in accounting for the gross aspects of the phase transition but failed to explain the transition entropy.

Kepler[19] measured the magnetic susceptibilities of the solid solutions $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3AsCH_3]_x{}^+(TCNQ)_2{}^{\overline{\cdot}}$ with seven different values of x in the range from 100 to 450 K and found a discontinuity at each transition point for all the materials except for the pure As-salt. The interesting feature is that the transition temperature T_c was raised with increasing x. Iida[26] examined also this relationship between x and T_c by use of a differential scanning calorimeter (DSC). He confirmed the same result and found that the entropy of transition decreases in proportion to x. As will be seen below, the present investigation leads to a quite different conclusion as to the x-dependence of the transition entropy.

Experimental

Materials. The P-salt was prepared according to the method of Melby *et al.*[27] The purified starting materials, methyltriphenylphosphonium iodide and TCNQ, were dissolved respectively into purified acetonitrile. Then these two solutions were mixed at about 70 °C with vigorous stirring under nitrogen atmosphere. After the reaction was over, the solution was kept quietly standing for 24 hours at a cool and dark place to give blackish prism crystals. The As-salt was

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prepared from purified methyltriphenylarsonium iodide and TCNQ by the same method with that of the P-salt. Three kinds of solid solutions$[(\mathrm{C_6H_5})_3\mathrm{PCH_3}]_{1-x}^{+}[(\mathrm{C_6H_5})_3\mathrm{AsCH_3}]_x^{+}$-$(\mathrm{TCNQ})_2^{\dot{-}}$ (x=0.159, 0.250, and 0.449) were obtained by the following procedures: Methyltriphenylphosphonium and methyltriphenylarsonium iodides were dissolved into pure acetonitrile in the ratio of $(1-x)$ to x. To this solution the acetonitrile solution containing the stoichiometric amount of TCNQ was added with vigorous stirring under nitrogen atmosphere at 70 °C.

TABLE 1. WEIGHT OF THE SAMPLE USED FOR HEAT CAPACITY MEASUREMENTS AND THE RESULTS OF ELEMENTARY ANALYSES[a] FOR $[(\mathrm{C_6H_5})_3\mathrm{PCH_3}]_{1-x}^{+}[(\mathrm{C_6H_5})_3$-$\mathrm{AsCH_3}]_x^{+}(\mathrm{TCNQ})_2^{\dot{-}}$

x	Weight/g	C/%	H/%	N/%	P/%
0.000	9.3395	75.43 (75.76)	3.81 (3.84)	16.44 (16.44)	4.82 (4.52)
0.159	11.5078	74.06 (74.56)	3.72 (3.78)	17.45 (16.18)	—
0.250	4.8597	74.36 (74.13)	3.63 (3.76)	16.62 (16.08)	3.68 (3.33)
0.449	11.0887	72.77 (73.21)	3.50 (3.72)	16.76 (15.88)	—
1.000	12.1251	70.96 (70.78)	3.37 (3.59)	15.45 (15.36)	—

a) The figures in parentheses are the values expected from the initial composition of the starting materials.

The results of elementary analyses for the five kinds of specimens are given in Table 1. The arsonium concentration x in each specimen was simply estimated from the amounts of the starting materials. The estimated values seem to approximate well to the true ones because Table 1 indicates that the composition of each specimen is simply proportional to the initial composition of the starting materials.

Measurements of Heat Capacities and Infrared Spectra. Heat capacity measurements of these radical salts were made with adiabatic calorimeters[28,29] in the temperature region from 12 to 370 K. The sample was sealed into the calorimeter cell with a small quantity of helium gas as a heat exchanger. The amounts of the samples used for the measurements are given in Table 1.

Infrared absorption spectra were recorded on a Grating-type Infrared Spectrophotometer Model DS-402G(Japan Spectroscopic Co., Ltd.) in the wave number region from 400 to 4000 cm^{-1}. Nujol mull and KBr-disk methods were employed for the preparation of samples. Far infrared absorption spectra of these radical salts were obtained by using a Spectrophotometer Model FIS-001 (Hitachi Ltd.) in the range from 30 to 400 cm^{-1}. Nujol mull method could not be used at high temperatures, so the sample was mixed with a small amount of polyethylene having low melting point.

Results

Heat Capacities. Heat capacity measurements were made for five kinds of solid solutions $[(\mathrm{C_6H_5})_3$-$\mathrm{PCH_3}]_{1-x}^{+}[(\mathrm{C_6H_5})_3\mathrm{AsCH_3}]_x^{+}(\mathrm{TCNQ})_2^{\dot{-}}$($x$=0, 0.159, 0.250, 0.449, and 1) in the temperature range from 12 to 370 K. The observed heat capacities for the salts with x=0.159, 0.250, 0.449, and 1 are plotted in Fig. 1, while the heat capacity of the pure P-salt (x=0) has been given in a previous paper.[3] The numerical values of the heat capacities for the P- and the As-salts are summarized in Table 2 and their standard thermodynamic quantities are given in Table 3.

The P-salt and the solid solutions exhibited the phase transition phenomenon at T_c=315.65 K (x=0), 325.80 K (x=0.159), 333.05 K (x=0.250), and 357.92 K (x= 0.449). In the case of the pure As-salt, however, any heat capacity anomaly due to a phase transition was not observed in the temperature region investigated. The phase transition temperature T_c was regularly raised with increasing x and the heat capacity anomaly concerning the phase transition of the solid solution was very sharp as that of the pure P-salt. From these two facts we can imagine that random mixing of the phosphonium and the arsonium cations is established and that the present specimens can be regarded as complete solid solutions.

The enthalpy and the entropy of transition were estimated by subtracting plausible normal heat capacities from the overall ones. In each case the normal heat capacity extrapolated from the high temperature phase was smaller than that of the low temperature phase at the transition point. The values of transition enthalpy ΔH and entropy ΔS thus obtained and also the jump of normal heat capacity ΔC_p detected at T_c are given in Table 4.

The heat capacities in the temperature region far below the transition points have a tendency to increase with increasing fraction x of the As-salt.

Infrared Absorption Spectra. In order to examine the influence of the phase transition we measured the infrared spectra of the P-salt both of the low and the high temperature phases. The spectra of both phases resembled closely each other except for minor changes in position and intensity of the absorption peaks. Figure 2 illustrates the far infrared spectra for the P-salt at 15 °C (=T_c−27.5 K), 40 °C (=T_c−2.5 K), and 80 °C (=T_c+37.5 K). In this wave number region only appreciable changes were observed at 320, 220, and 40 cm^{-1}. The band at 320 cm^{-1} vanished above T_c while a new band appeared at 40 cm^{-1}. The intensity of the band at 220 cm^{-1} was diminished above T_c. As a whole, it may be concluded that the phase transition phenomenon scarcely affected the infrared active modes of normal vibrations. This fact coincides well with the X-ray structural analyses,[4,5] which demonstrate that crystal structures of both the low and the high temperature modifications of the P-salt are triclinic system with the space group P$\bar{1}$.

Figure 3 represents the composition dependence of the infrared spectra for five kinds of materials in the wave number region from 1100 to 600 cm^{-1} at room temperature. The absorption bands at 710 and 900 cm^{-1} can safely be assigned to the phosphonium species since the intensities are proportional to the phosphonium concentration $(1-x)$. The band at 884 cm^{-1} is characteristic of the arsonium species because its intensity changes in proportion to the arsonium concentration x. Similar band arising from the arsonium species was observed in the far infrared region at 347 cm^{-1}. On the other hand, a new absorption peak was observed at

TABLE 2. HEAT CAPACITIES OF $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^{\cdot -}$ AND $[(C_6H_5)_3AsCH_3]^+(TCNQ)_2^{\cdot -}$

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
The P-SALT									
12.22	17.90	61.14	233.22	148.85	474.53	259.06	755.99	314.37	1243.8
13.33	22.62	64.32	245.16	153.43	486.16	263.53	767.58	315.38	1590.0
14.44	26.15	67.53	255.86	158.49	499.61	268.09	776.85	315.76	1619.9
15.70	30.16	71.44	267.48	164.00	513.65	272.77	789.34	316.03	1516.3
17.02	36.85	75.96	279.70	169.43	527.06	277.38	800.90	316.25	1506.0
18.46	43.83	80.28	292.21	174.77	540.68	279.63	806.58	316.61	1231.3
19.97	51.31	84.44	305.24	180.03	552.73	281.91	811.58	317.23	1102.3
21.43	57.96	88.62	317.40	184.22	567.07	285.84	821.92	318.02	978.17
22.91	64.69	92.82	328.79	197.49	593.43	291.94	838.36	318.84	927.10
24.80	73.78	96.92	339.72	200.05	599.46	297.09	850.68	319.68	914.83
27.01	85.07	100.96	349.90	204.63	611.96	298.00	855.25	321.36	912.46
29.20	95.92	102.83	354.72	209.64	624.40	301.76	863.95	322.41	910.70
31.40	107.03	106.08	363.66	214.58	637.23	303.06	868.11	324.08	911.10
33.65	118.38	109.90	373.65	219.44	650.44	305.54	874.33	326.72	911.02
36.29	131.21	114.25	385.41	224.26	662.14	306.82	880.40	330.38	913.88
39.28	145.09	119.12	400.41	229.00	675.46	308.88	909.41	334.89	926.86
42.27	158.46	122.12	405.92	230.88	680.00	310.08	942.85	340.03	939.94
45.32	171.33	125.06	413.90	235.73	698.14	310.84	955.23	345.37	948.94
48.45	184.19	129.86	426.34	240.52	708.49	311.52	962.34	350.67	965.47
51.61	197.08	134.76	438.49	245.24	722.86	312.12	962.80		
54.77	209.40	139.54	451.39	249.91	734.29	312.72	997.19		
57.95	221.36	144.23	463.12	254.51	745.40	313.30	1061.8		
The As-SALT									
14.06	24.81	54.59	224.78	108.21	398.73	168.34	561.66	251.57	764.71
15.22	30.01	57.29	235.17	111.17	406.62	173.10	573.89	256.42	777.52
16.33	35.53	60.47	247.30	114.08	414.99	177.80	585.78	262.01	790.57
17.69	42.79	60.81	248.90	116.95	423.06	182.46	598.04	267.11	806.07
19.26	51.18	64.09	260.82	120.13	431.60	187.08	608.87	268.34	807.21
20.82	59.29	67.53	273.60	123.60	440.17	191.80	622.57	270.99	812.55
22.33	67.31	70.80	284.93	127.03	450.17	196.66	634.73	275.60	823.12
23.83	75.27	73.95	295.27	130.41	459.23	201.46	647.23	280.21	829.71
25.59	84.58	76.99	305.39	130.74	459.53	206.21	658.92	284.77	842.78
27.59	95.10	79.93	314.98	133.43	468.26	210.91	671.37	289.32	849.35
29.48	105.42	82.61	322.93	136.53	475.97	215.56	686.01	294.04	864.55
31.28	114.99	82.79	323.97	139.93	485.07	216.98	679.36	298.88	878.67
33.17	125.20	85.58	332.23	143.29	493.63	219.91	691.96	304.51	890.86
35.46	137.00	85.72	332.72	146.93	503.60	221.91	691.55	310.99	908.64
38.00	149.47	89.18	343.20	150.95	514.40	222.88	694.30	317.52	922.44
40.65	161.72	92.54	353.56	155.00	524.50	226.88	724.30	324.00	938.35
43.45	175.68	95.82	363.00	159.01	532.79	231.79	714.59	330.46	956.78
46.23	188.91	99.01	372.78	160.48	540.69	236.76	726.80	336.88	974.17
49.00	200.84	102.14	380.95	162.98	545.74	241.75	740.80	343.29	998.48
51.78	212.57	105.21	390.15	163.77	550.45	246.68	752.30	349.73	1016.4

TABLE 3. STANDARD THERMODYNAMIC FUNCTIONS OF $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^{\cdot -}$ AND $[(C_6H_5)_3AsCH_3]^+(TCNQ)_2^{\cdot -}$

T/K	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$(H^\circ - H_0^\circ)/T$/J K^{-1} mol^{-1}	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$(H^\circ - H_0^\circ)/T$/J K^{-1} mol^{-1}
		the P-salt			the As-salt	
20	50.48	22.358	16.012	55.24	23.146	16.731
30	100.00	52.031	35.634	108.46	55.478	38.333
40	148.22	87.586	57.915	159.34	93.778	62.338
50	190.64	125.30	80.291	205.26	134.36	86.418
60	228.86	163.49	101.92	245.62	175.40	109.63
70	263.34	201.48	122.63	282.02	216.08	131.73
80	292.05	238.49	141.99	314.76	255.92	152.61
90	321.17	274.60	160.30	345.88	294.81	172.38
100	347.42	309.79	177.70	375.44	332.80	191.22
120	400.74	377.85	210.43	431.28	406.24	226.63
140	452.34	443.48	241.29	485.34	476.77	259.71
160	503.29	507.19	270.84	538.83	545.05	291.24
180	552.74	569.38	299.47	591.63	611.60	321.72
200	599.83	630.01	327.11	643.42	676.60	351.29
220	651.42	689.59	354.23	692.22	740.20	380.05
240	706.80	748.57	381.23	734.92	802.13	407.71
260	758.26	807.29	408.36	785.72	862.98	434.86
280	807.32	865.25	435.08	833.68	922.97	461.64
300	859.26	922.69	461.60	879.74	982.05	487.97
320	915.30	984.36	492.55	929.76	1040.4	514.01
340	939.70	1040.1	517.67	983.60	1098.4	540.02
360	989.00	1095.2	542.48	1039.7	1156.2	566.22
370	1013.5	1122.6	554.88	1067.7	1185.0	579.39

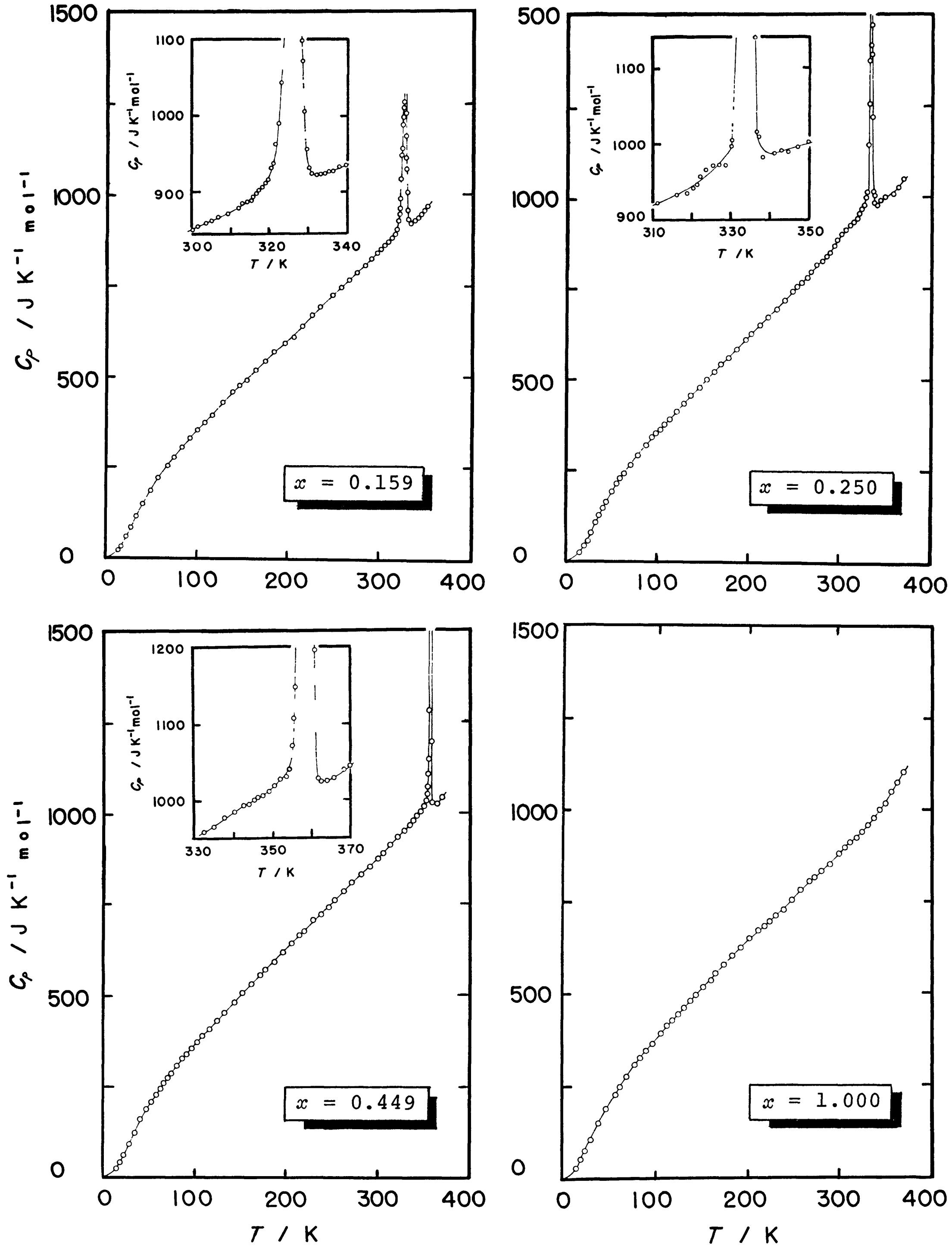

Fig. 1. Molar heat capacity of $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\overline{\cdot}}$ (x=0.159, 0.250, 0.449, and 1.000).

Table 4. Thermodynamic quantities related to the phase transition of the solid solutions $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\overline{\cdot}}$

x	T_C / K	ΔC_p / J K^{-1} mol^{-1}	ΔH / J mol^{-1}	ΔS / J K^{-1} mol^{-1}
0.000	315.65	−15.8	2030	6.431
0.159	325.80	−11.7	2028	6.224
0.250	333.05	−6.3	1967	5.905
0.449	357.92	−8.0	1927	5.383

860 cm^{-1} only when the specimen formed the solid solution. As the crystal structures of the P- and the As-salts are isomorphous at room temperature,[4] this new band may correspond to the boundary mode between the phosphonium and the arsonium cations.

Phase Transition of the P-salt

As was described in a previous section, the normal heat capacity of the high temperature phase was 15.75

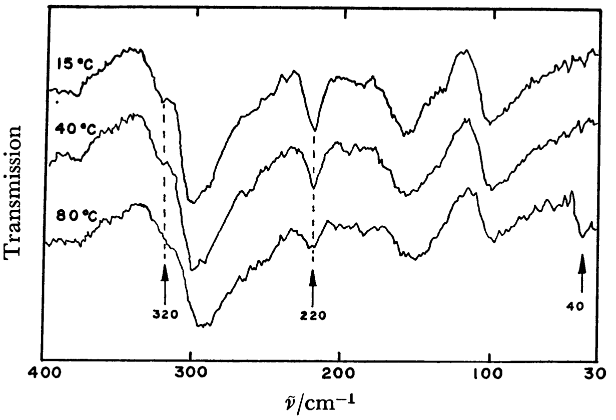

Fig. 2. Far infrared spectra of $[(C_6H_5)_3PCH_3]^+$-$(TCNQ)_2{}^{\bar{\cdot}}$ in the wave number region from 400 to 30 cm^{-1} at three different temperatures (T_C=42.50 °C).

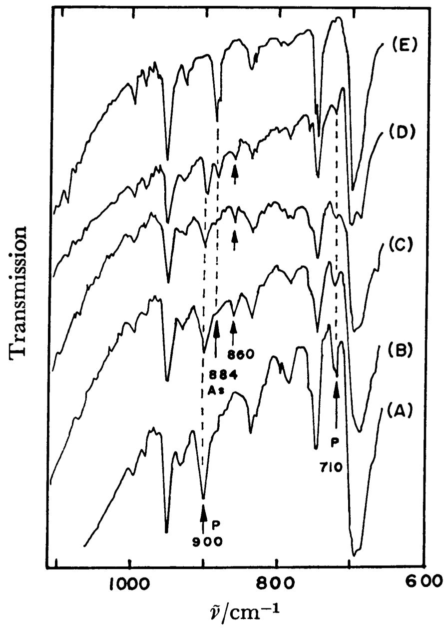

Fig. 3. Infrared spectra of $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3$-$AsCH_3]_x{}^+(TCNQ)_2{}^{\bar{\cdot}}$ in the wave number region from 1100 to 600 cm^{-1} at a room temperature. (A) x=0.000, (B) x=0.159, (C) x=0.250, (D) x=0.449, and (E) x=1.000.

J K^{-1} mol^{-1} smaller than that of the low temperature phase at T_C. This fact implies that the excitation of phonons is easier in the low- than in the high-temperature phase at least in the vicinity of T_C. This situation seems to be related with the contraction of crystal volume[5,20] at T_C.

The enthalpy and the entropy of transition were determined to be 2030 J mol^{-1} and 6.431 J K^{-1} mol^{-1}, respectively. The entropy corresponds to R ln 2.12. This value cannot be explained solely by the contribution from the elctronic spin freedom. We discuss below a problem what kinds of freedoms contribute to the phenomenon of the phase transition.

(1) Contribution of Magnetic Spin Freedom. The magnetic spin in this radical salt is known to behave just like being in the singlet-triplet equilibrium.[7,8,22] The contribution of the magnetic spin system to the entropy of transition can be estimated from the triplet density defined by

$$\rho \equiv \left\{1+\frac{1}{3}\exp(J/kT)\right\}^{-1}, \tag{1}$$

where J is the energy difference between a singlet ground state and an excited triplet state. The temperature dependence of ρ is obtained from the magnetic susceptibility measurements[19] as the paramagnetic contribution to the susceptibility can be fitted approximately to the expression

$$\chi = \frac{NS(S+1)g^2m_B{}^2}{3kT}\left\{1+\frac{1}{3}\exp(J/kT)\right\}^{-1}, \tag{2}$$

where g is the electronic g-factor, m_B the Bohr magneton, S the spin quantum number and N the number of quasimolecules. By assuming g=2.0, S=1 and $N=N_A/2$ (N_A is the Avogadro constant), we obtain the relation

$$\chi T = 0.5002\rho. \tag{3}$$

The entropy arising from the spin system corresponds to

$$S = \frac{1}{2}R\{\rho \ln 3 - \rho \ln \rho - (1-\rho)\ln(1-\rho)\}. \tag{4}$$

Since the triplet density is zero at 0 K and 3/4 at infinite temperature, the total spin entropy amounts to R ln 2(=5.763 J K^{-1} mol^{-1}). However, the observable magnetic entropy as the transition entropy is limited to only a small part of R ln 2 and the remaining part is smeared over a wide temperature region as the Schottky-type anomaly, because the present phase transition is characterized by a small jump of the magnetic susceptibility[19] and thus a small change in ρ. By using Kepler's data,[19] the contribution of the spin entropy to the phase transition was estimated to be 1.93 J K^{-1} mol^{-1}. Since the anomalous heat capacity has its skirt below T_C, the calculation is made based on the change in ρ over the temperature range corresponding to the heat capacity anomaly.[30] At any rate, the estimated magnetic entropy merely corresponds to thirty percent of the total entropy of transition. Therefore, the remaining entropy of transition due to other origins amounts to 4.50 J K^{-1} mol^{-1}. On the other hand, if the system be allowed to include a considerable fraction of doublet as well as the singlet-triplet equilibrium, the transition entropy due to the magnetic origin would become larger than 1.93 J K^{-1} mol^{-1}. The experimental evidence,[19] however, is not favorable to the existence of such a large amount of doublet in the temperature region investigated here.

(2) Contribution of Conduction Electrons. The electric conductivity of this radical salt[10] is abruptly increased at T_C. Increase in the number of conduction electrons will cause an increase in the entropy of the system. The energy gap between the conduction and the filled bands has been estimated to be 0.4 eV below T_C and 0.3 eV above it.[26] This difference leads to an increase in the excitation of conduction electrons in the high temperature phase. The energy gap, however, is about ten times larger than the thermal energy kT in the neighborhood of T_C. Accordingly the number of electrons which can be excited to the conduction band by the thermal energy is negligibly small and the

entropy gain due to such electrons is the order of magnitude of the present experimental error. Thus the freedom of conduction electrons cannot practically contribute to the entropy of transition.[31]

(3) Contribution of the Change in Lattice Structure. According to the recent structural analyses by Konno and Saito,[5] the conformations of the phosphonium cations are quite different each other in both the low- and the high-temperature phases, whereas the crystal structure and the space group are not changed by the phase transition. In the high temperature phase two of the three phenyl groups belonging to a phosphonium cation are rotated drastically by about 56 and 45° from the positions observed in the low temperature forms, and the interplanar distances in the TCNQ column are altered. These changes in the conformation and the packing geometry modify the distribution function of the lattice vibration to some extent. Accordingly, a part of the excess transition entropy other than the magnetic contribution may be attributable to this origin. The quantitative estimation of this effect is, however, not easy.

The interesting but peculiar feature concerning the high temperature phase is the existence of about ten percent of the phosphonium cations having the different configuration.[5] If it were the case, the entropy due to their mixing amounts to 2.70 J K^{-1} mol^{-1}. This corresponds to sixty percent of the remaining entropy other than the spin contribution.

Phase Transitions of Solid Solutions

In order to demonstrate clearly the composition dependence of heat capacities of the solid solutions, the heat capacity curves around T_c of the five samples are shown in Fig. 4. One of the interesting features is that the transition temperature was shifted toward the high temperature side with increasing fraction of the As-salt. If the solid solution is simply regarded as the P-salt being diluted with the As-salt, the composition dependence of the transition temperature seems to be quite curious. In general the effect of dilution would make the existing interaction weaker and thus would lead to a system having a lower transition temperature. In view of the fact, however, that it is not the cations but the $(TCNQ)_2^{\cdot-}$ anion radicals which are responsible for the magnetic spin system, the existence of the P-salt fraction should be regarded only as a trigger for the phase transition.

The transition enthalpy ΔH and the entropy ΔS

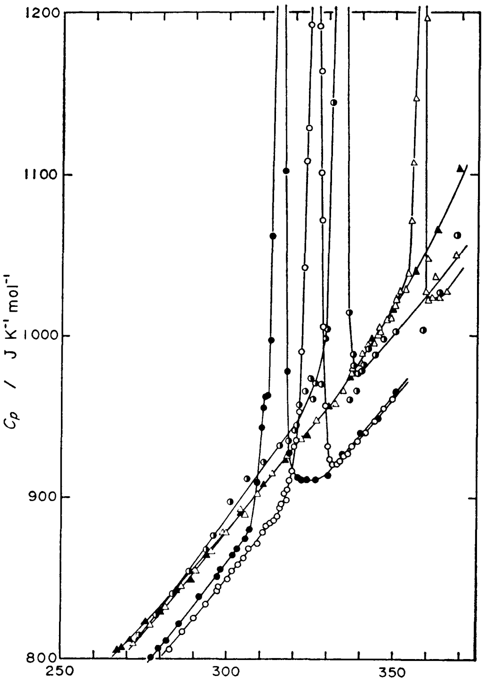

Fig. 4. Heat capacities of $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\cdot-}$ in the vicinity of T_C. (●) x=0.000, (○) x=0.159, (◑) x=0.250, (△) x=0.449, and (▲) x=1.000.

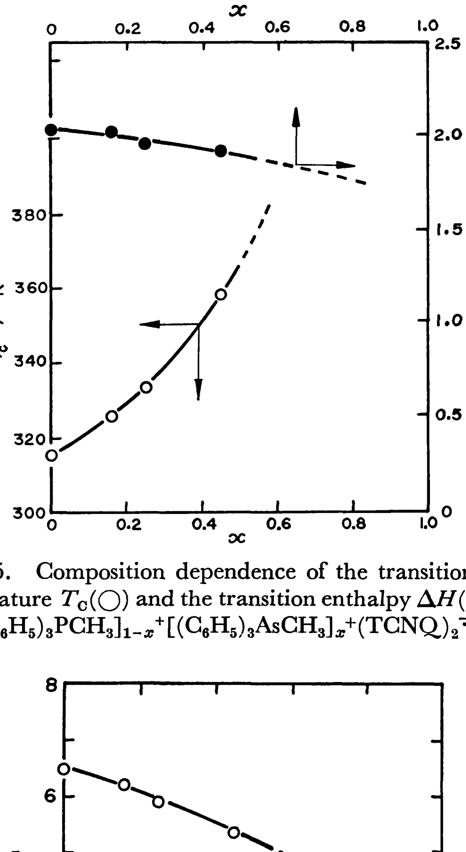

Fig. 5. Composition dependence of the transition temperature T_C(○) and the transition enthalpy ΔH(●) for $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\cdot-}$.

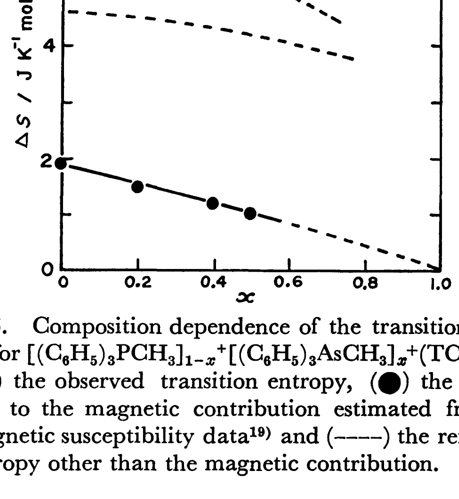

Fig. 6. Composition dependence of the transition entropy for $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\cdot-}$; (○) the observed transition entropy, (●) the entropy due to the magnetic contribution estimated from the magnetic susceptibility data[19] and (----) the remaining entropy other than the magnetic contribution.

determined from the heat capacity anomalies are plotted in Figs. 5 and 6, respectively, as a function of the As-salt fraction. Also shown in Fig. 5 is the composition dependence of the transition temperature. A remarkable feature is that the enthalpy and the entropy of transition do not seem to converge to zero when the As-salt fraction x approaches to unity. These results are quite different from the previous ones by Iida[26)] obtained with a differential scanning calorimeter(DSC). His results indicate that the ΔH and the ΔS are decreased linearly with x and finally vanished at $x=1$. The heat capacity anomaly due to the present phase transition becomes broader with increasing fraction of the As-salt and the contribution from the skirt of the heat capacity anomaly was increased. A shortcoming inherent in a thermal analysis by use of DSC is to fail in detecting a moderate thermal change and to truncate a heat capacity peak. Therefore, a simple thermal analysis has a risk to underestimate the enthalpy and the entropy of transition. The discrepancy between his results and ours may be due to these situations.

The entropy due to the magnetic contribution was estimated in a scheme of the singlet-triplet equilibrium. For this purpose, the magnetic susceptibilities of the solid solutions measured by Kepler[19)] were used to obtain the value of triplet density below and above the transition point. The results are shown in Fig. 6. As is in the case of the P-salt, the contribution from the magnetic spin system amounts to only twenty or thirty percent of the total entropy of transition. A remarkable feature found here is that the entropy other than the magnetic contribution is nearly independent of the composition of the solid solution. This fact suggests that the solid solution may undergo almost the same structural or geometrical change with that of the pure P-salt independently of the arsonium fraction. A favorable evidence for the structural change is the discontinuity of the normal heat capacity found at T_c (see Table 4).

According to the high-pressure experiment by Merkl *et al.*[20)] the transition temperatures of both the P- and the As-salts are lowered with increasing the external pressure although the As-salt does not show the corresponding phase transition at an atmospheric pressure because of its thermal decomposition. If the p-T diagram for the P-salt is extrapolated into the negative pressure region, the occurrence of a hypothetical phase transition would be possible at a temperature higher than 315.65 K where the P-salt undergoes the phase transition at 1 atm. The volume of the unit cell at negative pressure is considered to be slightly larger than that at 1 atm. According to the X-ray analyses for the P- and the As-salts at room temperature[4,5)] the lattice volume of the As-salt is slightly larger than that of the P-salt. Therefore it is plausible that the increase of the As-salt fraction in the solid solution will bring about the increase in the lattice volume. This effect just corresponds to the lattice expansion of the P-salt or in other words the negative pressure in the p-T diagram. This is one of the most probable reasons why the transition temperature is raised with the increase of the arsonium salt fraction.

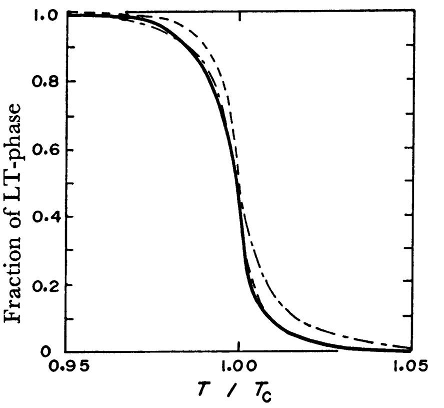

Fig. 7. Comparison of the low temperature fraction of the P-salt between the experiment and the theory (T_C= 315.65 K).
(——): The experimental value, (- - -): the calculated value for $(J_{LH}/N^{2/3})$ $=1.5\,kT_C$ and (N_A/N) = 100, (----): the calculated value for $(J_{LH}/N^{2/3})=1.5\,kT_C$ and $(N_A/N)=167$.

Table 5. The parameters determined by the “best” fit of the present model to the experimental values for $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\overline{\cdot}}$

x	0.000	0.159	0.250	0.449
$J_{LH}/(N^{2/3}kT_C)$	1.5	1.1	1.0	0.5
$N_A/N\,(T<T_C)$	100	125	200	100
$N_A/N\,(T>T_C)$	167	217	500	1430

In a previous paper,[33)] we presented a phenomenological model for the phase transition of potassium p-chloranil anion radical salt. The principle is virtually the same with the Frenkel theory of heterophase fluctuation in liquid.[34)] The parameters characteristic of this model are the number of cells or embryos, N, and the interaction energy between adjacent cells belonging to the low and the high temperature phases, J_{LH}. If the Avogadro constant is denoted as N_A, the ratio, (N_A/N), corresponds to the number of molecules included in a cell. The phase transition becomes a first order when $(J_{LH}/N^{2/3})>2kT_c$, while the phase transition is of a higher order when $(J_{LH}/N^{2/3})$ is equal to $2kT_c$. Figure 7 illustrates the “best” fit of this model to the experimental value for the P-salt. The “best” fit below T_c is obtained under the condition of $(J_{LH}/N^{2/3})=1.5\,kT_c$ and $(N_A/N)=100$ but above T_c it is necessary to adopt a large value of $(N_A/N)=167$ for the “best” fit. This tendency is found for all the phase transitions observed for the solid solutions (see Table 5). This suggests that the intermolecular correlation is different below and above T_C. It should be remarked here that as shown in Table 5, the “best” fit value of $J_{LH}/(N^{2/3}kT_c)$ becomes small with increasing the arsonium fraction x while the value of (N_A/N) increases with x. These results indicate that the cooperativeness of the phase transition becomes weak with increasing x and that the more the P-salt is diluted with the As-salt, the larger number of molecules is included in a correlation region in which the transition from the low to the high temperature modification takes place simultaneously.

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30) Iida[26] has reported the spin entropy of 0.55 J K^{-1} mol^{-1}. But this is underestimated because he has used only the first term of the right-hand side of Eq. 4.

31) It is interesting to note here that there still exists an example in which the conduction electrons considerably contribute to the entropy of a system. According to Epstein *et al.*[32] the Fermi temperature of *N*-methylphenazinium tetracyanoquinodimethanide is low enough to give an appreciable contribution of the conduction electrons to the entropy of the system even at a room temperature.

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