INFLUENCE OF IMPURITIES ON THE SINGULARITY OF THE THERMODYNAMIC POTENTIAL AT THE LIQUID-VAPOR CRITICAL POINT

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The specific heats C_V of air and nitrogen containing 1.2% impurities were measured near the critical point. The results are compared with those obtained earlier for pure substances.[1,2] It is found that, under the influence of impurities, the logarithmic singularity of C_V near the critical point is deformed and that the deformed $C_V(T)$ curves resemble the $C_p(T)$ curves for solids near the Curie point. It is suggested that a term proportional to the total number of impurities be introduced into the formula[8] obtained earlier for C_V.

AFTER the discovery of a singularity in the thermodynamic potential near the critical point of a pure substance, in the measurements of the specific heat C_V of argon and oxygen,[1,2] the problem arose of the deformation of this singularity under the influence of various factors.

One of the factors causing the singularity to broaden is the addition of impurities to a substance. In the present paper, we report the results of the measurements, near the critical points of the specific heats C_V of nitrogen containing a small amount of impurities (about 98.8 mol.% nitrogen, 0.7% oxygen, and $\approx 0.5\%$ argon), and of air (about 77.4% nitrogen, 21.7% oxygen, 0.9% argon).

The critical parameters of pure nitrogen and air are known.[3] In our experiments, the densities were 0.318 g/cm³ for the air, which was 0.6% less than the critical value, and 0.311 g/cm³ for the impure nitrogen, which was equal to the critical density of pure nitrogen. The latter should be very close to the critical density of the investigated impure nitrogen because the impurity content was not high and the difference between the critical density of air and nitrogen is only about 3%.

We adopted the method described in [4,5]. The use of a potentiometer type R-308 with a photomultiplier type F-305 in the temperature measuring circuit made it possible to reduce temperature variations in the calorimeter itself (5×10^{-4} – 2×10^{-3} deg/hr in the most important cases) and to determine the temperature more reliably. All this increased the precision of the experiment (the scatter of the experimental points did not exceed 10% over the whole range of temperatures, decreasing to 1% away from the singularities, for measurements in steps of ΔT up to 0.05 deg K).

It is very important to establish equilibrium at the critical point. In the immediate vicinity of the critical point the time for the establishment of equilibrium in pure substances (argon, oxygen) is usually 3—4 hours. It was found that near the critical point of a mixture this time increased to 5—6 hours when the components were mixed continuously throughout the experiment. This confirmed the recommendations of other experimenters[6] to increase the time taken to homogenize mixtures, compared with pure substances.

The data obtained are presented in Fig. 1 and in Tables I and II. For comparison, Fig. 1 includes the specific heat curve of pure oxygen near its critical point.[2] Figure 1 itself shows that the temperature dependence of C_V of air is very characteristic. The discontinuity and the specific-heat maximum are clearly separated.
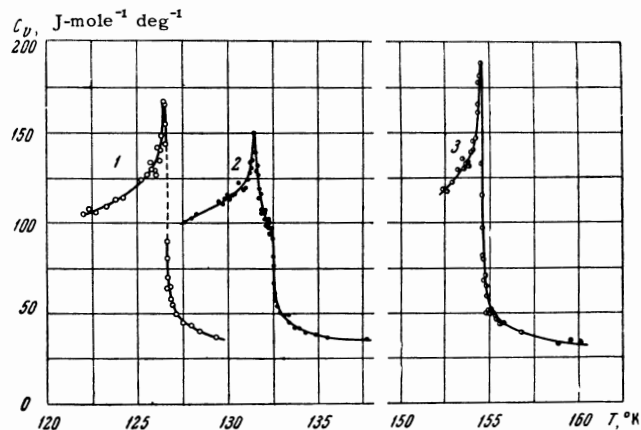
The same effect was observed in the nitrogen

FIG. 1. Temperature dependence of the specific heat C_V: 1) N_2 + 1.2% impurities, $\rho = 0.311$ g/cm³; 2) air, $\rho = 0.318$ g/cm²; 3) O_2, $\rho = 0.408$ g/cm³.

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Table I. Specific heat of nitrogen (ρ = 0.311 g/cm^3)

T, °K	ΔT, °K	C$_v$, J-mole^{-1} deg^{-1}	T, °K	ΔT, °K	C$_v$, J-mole^{-1} deg^{-1}	T, °K	ΔT, °K	C$_v$, J-mole^{-1} deg^{-1}
123.80	0.438	112.9	126.62	0.175	89.7	126.18	0.491	135.1
124.22	0.439	114.3	127.10	0.139	50.3	126.44	0.059	168.0
125.24	0.270	124.4	127.54	0.189	45.3	126.53	0.062	154.6
125.53	0.266	126.8	127.91	0.378	42.8	126.62	0.077	81.2
125.78	0.195	129.9	128.44	0.594	39.8	126.73	0.072	65.2
125.94	0.230	129.8	129.31	1.096	36.6	126.66	0.054	64.5
125.98	0.197	126.7	125.71	0.225	134.4	126.80	0.074	57.6
126.09	0.121	142.0	122.03	0.403	104.8	126.96	0.095	55.0
126.17	0.120	141.0	122.27	0.231	107.5	126.53	0.044	143.4
126.31	0.115	148.6	122.69	0.700	106.2	126.64	0.063	70.3
126.45	0.115	165.8	123.34	0.685	108.8	126.73	0.066	64.9

containing impurities, but it can be seen only on the semilogarithmic scale (Fig. 2). Here, we assumed T'_c to be the temperature of the specific heat maximum (T'_c = 126.47° for impure nitrogen and T'_c = 131.41°K for air). The discontinuity obviously corresponded to the critical temperature of the mixture. Thus, for air, we obtained T_d = 132.53°K, which was very close to the tabulated value T_c = 132.46°K.[7]

It is clear from Fig. 2 that the lower the impurity content in a substance, the closer the rise of the specific-heat C_v is to the logarithmic rise observed in a pure substance. The presence of impurities slows down this rise and results in a finite value of C_v. The discontinuity of the specific heat C_v corresponds to the critical temperature of the mixture, while the maximum (peak) represents the trace of the logarithmic singularity, characteristic of a pure substance but displaced as well as deformed by the presence of impurities.

We may draw the following quantitative conclusions about the influence of impurities on the thermodynamic potential singularity. The addition of 1.2% impurities to pure nitrogen (T_c = 126.16°K) causes a shift of the specific heat maximum by 0.31 deg, while the presence of 22.6% impurities gives $T'_c - T_c$ = 5.35 deg, i.e., the shift $t = (T'_c - T_c)/T_c$ is approximately proportional to the total number of impurities. This means
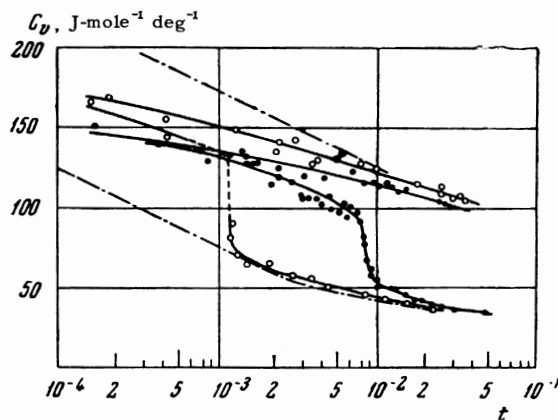

FIG. 2. Dependence of the specific heat C_v on the quantity $t = (T - T'_c)/T'_c$: o — N$_2$ + 1.2% impurities; ● — air; chain curves represent O$_2$.

Table II. Specific heat of air (ρ = 0.318 g/cm^3)

T, °K	ΔT, °K	C$_v$, J-mole^{-1} deg^{-1}	T, °K	ΔT, °K	C$_v$, J-mole^{-1} deg^{-1}	T, °K	ΔT, °K	C$_v$, J-mole^{-1} deg^{-1}
127.93	0.224	103.0	131.39	0.098	150.8	132.29	0.065	100.8
128.18	0.295	105.1	131.46	0.052	139.7	132.39	0.071	97.2
129.43	0.275	111.9	131.52	0.055	128.8	132.42	0.080	91.8
129.55	0.202	100.7	131.60	0.113	127.3	132.48	0.122	81.9
129.65	0.221	110.6	131.65	0.061	132.2	132.50	0.086	77.2
129.80	0.156	113.5	131.69	0.093	113.8	132.53	0.091	67.5
129.93	0.254	115.7	131.72	0.119	119.2	132.61	0.103	57.7
130.05	0.156	113.5	131.79	0.091	116.4	132.62	0.151	61.4
130.18	0.154	115.5	131.84	0.130	107.8	132.71	0.107	54.3
130.33	0.205	116.0	131.84	0.198	106.0	132.89	0.141	50.8
130.50	0.201	122.7	131.89	0.098	106.0	133.03	0.422	49.4
130.81	0.121	118.8	131.95	0.105	105.5	133.11	0.182	48.8
130.96	0.126	119.7	132.00	0.136	102.3	133.38	0.231	45.4
131.10	0.117	124.7	132.06	0.037	107.5	133.69	0.324	42.2
131.18	0.056	128.1	132.03	0.066	98.7	133.94	0.161	42.1
131.20	0.065	128.1	132.15	0.069	97.6	134.30	0.308	40.0
131.22	0.054	134.5	132.16	0.070	97.2	134.80	0.631	38.5
131.26	0.055	130.7	132.22	0.064	102.7	135.48	0.650	36.6
131.31	0.053	135.4	132.24	0.072	94.2	137.69	0.403	34.3

that we must, first of all, introduce into the logarithmic part of the thermodynamic potential[8] a term δX proportional to the impurity concentration, where $\delta \approx 0.2$, according to the results of our experiments.

It is interesting to compare the results obtained here with the measurements of the specific heat C_p of solids near the Curie point. It is found that our curves, deformed by the presence of impurities, resemble the corresponding curves for C_p of solids, in which the presence of imperfections (at least in the form of structural defects) is unavoidable. Figure 3 shows the $C_p(T)$ curve for MnS.[9] Similar results have been obtained in our laboratory for gadolinium containing impurities.[10] Very recently, a similar dependence of C_p on T was reported by Skalyo and Friedberg for the antiferromagnetic transition in $CoCl_2 \cdot 6H_2O$ at helium temperatures.[11]
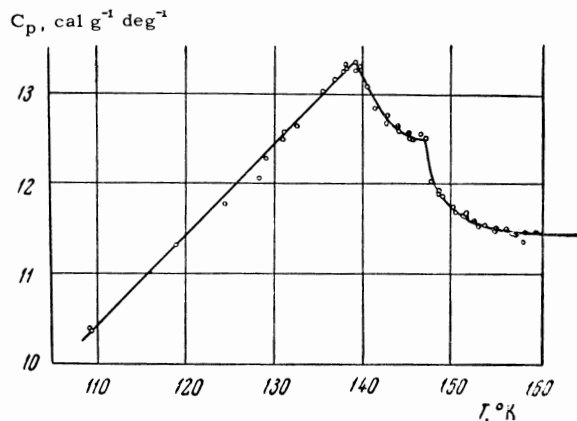
C_p, cal g^{-1} deg^{-1}

FIG. 3. Temperature dependence of the specific heat C_p for MnS.[9]

This singularity is not accidental. The nature of the deformation of the singularity of C_v due to the presence of impurities in our experiments allows us to understand the basic features of the singularity in the dependence of $C_p(T)$ for ferromagnets and antiferromagnets near the Curie point.

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