

Tables for Use in the Interpretation of Paramagnetic Behavior Below 1° K; for the Chromic Alums ($J=3/2$)

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The method of interpreting susceptibility and entropy data, obtained in adiabatic demagnetization experiments, by means of the theory of Hebb and Purcell in order to derive absolute temperatures is recounted briefly. This forms an introduction to tables that enable one to carry out this procedure for the case of the chromic alums.

The low-temperature behavior of the chromic alums is largely determined by the fact that the fourfold degenerate ground level of the Cr^{+++} ion is split by the crystalline electric field (Stark effect) into two doublets separated by an energy δ . The theory of Hebb and Purcell [1]¹ yields expressions for the susceptibility, χ_0 , and the entropy, S , as functions of the absolute temperature, T , and this splitting δ . Thus one may obtain a relation between S and χ_0 for any chosen δ . In practice one usually employs the "magnetic temperature" T^* instead of χ_0 , and $T^*=c/\chi_0$, where c is the Curie constant per cubic centimeter.

Now experiment also leads to a χ_0 versus S (or T^* versus S) relation, for S may be calculated quite accurately, simply from the conditions of magnetic field and temperature at the beginning of the isentropic demagnetization process, and χ_0 is measured at the end. One therefore has only to find that value of δ which leads to an S versus T^* curve fitting the experimental points. Then over the range of agreement one may suppose the Hebb and Purcell $\chi_0(T)$ and $S(T)$ formulas to be individually correct, and the former leads at once to the establishment of the absolute temperatures.

Table 1 gives, effectively, corresponding values of T/δ and T^*/δ calculated from the Hebb and Purcell

TABLE 1. Corresponding values of kT/δ and $k(T^*-T)/\delta$ calculated from the Hebb and Purcell [1] formula: $T^*/\delta=\gamma^{-1}\times T/\delta$ (see text)

kT/δ	$\frac{T^*-T}{\delta/k}$	kT/δ	$\frac{T^*-T}{\delta/k}$	kT/δ	$\frac{T^*-T}{\delta/k}$
0.05	0.0281 ₃	1.0	0.0312 ₅	3.0	0.0110 ₃
.10	.0470 ₆	1.1	.0287 ₂	3.2	.0103 ₅
.15	.0584 ₂	1.2	.0265 ₅	3.4	.0097 ₄
.20	.0639 ₀	1.3	.0246 ₇	3.6	.0092 ₂
.25	.0653 ₄	1.4	.0230 ₃	3.8	.0087 ₁
.30	.0643 ₁	1.5	.0215 ₉	4.0	.0083 ₁
.35	.0619 ₇	1.6	.0203 ₀	4.2	.0079 ₀
.40	.0590 ₁	1.7	.0191 ₇	4.4	.0075 ₄
.45	.0558 ₅	1.8	.0181 ₄	4.6	.0072 ₂
.50	.0527 ₁	1.9	.0172 ₂	4.8	.0069 ₃
.55	.0497 ₁	2.0	.0163 ₉	5.0	.0066 ₄
.60	.0469 ₁	2.1	.0156 ₃		
.65	.0443 ₂	2.2	.0149 ₄		
.70	.0419 ₃	2.3	.0143 ₁		
.75	.0397 ₅	2.4	.0137 ₃		
.80	.0377 ₅	2.5	.0131 ₅		
.85	.0359 ₁	2.6	.0127 ₀		
.90	.0342 ₃	2.7	.0122 ₃		
.95	.0326 ₃	2.8	.0118 ₀		
1.00	.0312 ₅	2.9	.0113 ₉		
		3.0	.0110 ₃		

¹ Figures in brackets indicate the literature references at the end of this paper.

formula [1]: $T^*/\delta=\gamma^{-1}\times T/\delta$, where

$$\gamma = \frac{0.2}{1+e^{-\delta/kT}} \left[\left(3 + \frac{4kT^*}{\delta} \right) + \left(3 - \frac{4kT}{\delta} \right) e^{-\delta/kT} \right]. \quad (1)$$

Tables 2 to 5 contain the data necessary for calculating the "experimental entropy," that is, in the magnetic field at the initial temperature, and the field-free entropy as a function of kT/δ .

Considering first the case of the entropy in zero field and at low temperatures, two effects contribute to a reduction in the entropy below the "ideal" value of $R \log_e 4$, namely, the Stark splitting and magnetic interaction. The theory treats these two contributions separately, and they are additive. The "Stark entropy" is calculated from the partition function, $Z_c=2(1+e^{-\delta/kT})$, and is given in table 2. Table 3 lists as a function of x (where $x=kT/\delta$), the quantity $(d/dx)(\Omega/x)$, Ω being as defined in reference [1]. The magnetic entropy, S_m , is then given by

$$S_m/R = (\tau/\delta)^2 \frac{d}{dx} \left(\frac{\Omega}{x} \right), \quad (2)$$

where $\tau/k=3c(=0.0211$ deg and 0.0194 deg for the potassium and methylammonium alums, respectively). Hence

$$\log_e 4 - S/R = (\log_e 4 - S/R)_{\text{Stark}} + S_m/R.$$

TABLE 2. "Stark entropy", or the reduction in entropy below the value $R \log_e 4$, caused by the effect of the crystal field

kT/δ	$\log_e 4 - S/R$	kT/δ	$\log_e 4 - S/R$	kT/δ	$\log_e 4 - S/R$
0	0.6931 ₃	1.0	0.1109 ₄	3.0	0.0137 ₀
0.05	.6931 ₃	1.1	.0935 ₃	3.2	.0120 ₆
.10	.6926 ₅	1.2	.0798 ₁	3.4	.0107 ₀
.15	.6834 ₆	1.3	.0688 ₃	3.6	.0095 ₃
.20	.6529 ₇	1.4	.0599 ₃	3.8	.0085 ₃
.25	.6030 ₃	1.5	.0526 ₂	4.0	.0077 ₃
.30	.5432 ₃	1.6	.0465 ₄	4.2	.0070 ₄
.35	.4821 ₂	1.7	.0414 ₅	4.4	.0064 ₂
.40	.4246 ₁	1.8	.0371 ₄	4.6	.0058 ₇
.45	.3729 ₆	1.9	.0334 ₆	4.8	.0054 ₀
.50	.3278 ₁	2.0	.0303 ₀	5.0	.0049 ₃
.55	.2888 ₁	2.1	.0275 ₆		
.60	.2553 ₃	2.2	.0251 ₇		
.65	.2267 ₀	2.3	.0230 ₃		
.70	.2021 ₄	2.4	.0212 ₄		
.75	.1810 ₄	2.5	.0196 ₁		
.80	.1628 ₄	2.6	.0181 ₅		
.85	.1470 ₃	2.7	.0168 ₆		
.90	.1333 ₃	2.8	.0156 ₆		
.95	.1214 ₃	2.9	.0146 ₅		
1.00	.1109 ₄	3.0	.0137 ₀		

TABLE 3. Corresponding values of kT/δ and the function $(d/dx)(\Omega/x)$ [1]

The "magnetic entropy", S_m , or the entropy diminution additional to the Stark entropy (table 2), is obtained from the relation $S_m/R = (\tau/\delta)^2 (d/dx)(\Omega/x)$, (see text).

kT/δ	$\frac{d}{dx} \left(\frac{\Omega}{x} \right)$	kT/δ	$\frac{d}{dx} \left(\frac{\Omega}{x} \right)$	kT/δ	$\frac{d}{dx} \left(\frac{\Omega}{x} \right)$
0	-----	1.0	0.7706 ₉	3.0	0.1228 ₃
0.05	-----	1.1	.6795 ₁	3.2	.1090 ₂
.10	7.1616 ₆	1.2	.6005 ₆	3.4	.0971 ₅
.15	2.9618 ₇	1.3	.5327 ₁	3.6	.0871 ₀
.20	1.4571 ₈	1.4	.4745 ₃	3.8	.0785 ₂
.25	0.9478 ₈	1.5	.4245 ₆	4.0	.0711 ₄
.30	.8777 ₇	1.6	.3817 ₆	4.2	.0647 ₄
.35	.9611 ₈	1.7	.3444 ₃	4.4	.0591 ₇
.40	1.0705 ₆	1.8	.3122 ₁	4.6	.0542 ₆
.45	1.1518 ₇	1.9	.2841 ₁	4.8	.0499 ₃
.50	1.1940 ₆	2.0	.2595 ₀	5.0	.0461 ₃
.55	1.2007 ₆	2.1	.2378 ₃		
.60	1.1820 ₆	2.2	.2187 ₆		
.65	1.1451 ₃	2.3	.2017 ₃		
.70	1.0967 ₆	2.4	.1866 ₇		
.75	1.0425 ₈	2.5	.1731 ₃		
.80	0.9857 ₃	2.6	.1610 ₆		
.85	.9292 ₀	2.7	.1500 ₉		
.90	.8738 ₈	2.8	.1402 ₃		
.95	.8208 ₃	2.9	.1313 ₀		
1.00	.7706 ₆	3.0	.1228 ₃		

Table 4 lists values of the entropy, for corresponding values of H/T , calculated by means of the "Brillouin formula." For the case $J=3/2$, one has

$$(S/R)_B = a \coth a - 4a \coth 4a + \log_e \sinh 4a - \log_e \sinh a, \quad (3)$$

where $a = \mu H/kT$; μ is the Bohr magneton, 9.271×10^{-21} emu, and k is the Boltzmann constant, 1.3805×10^{-16} erg deg⁻¹.

In order to derive an accurate value of δ , however, one must take cognizance of the fact that the Brillouin entropy (table 4) is only appropriate to the ideal case of a fourfold degenerate ground level. The effect of the crystalline electric field is to modify the pattern of the level splitting in a magnetic field, and for small fields the correction, $\Delta S/R$, to be

applied to the entropy reduction, $\log_e 4 - S_B/R$, is relatively large.

An entropy formula has been derived [3] that takes this effect into account, but it is more unwieldy than the Brillouin formula (a straightforward function of H/T) as it is a function of H , T , and δ . For the chromic alums the value of δ/k is always close to 0.25 deg, and starting temperatures (that is, bath temperatures) will, in general, be of the order of 1.1° to 1.2° K. Because $\Delta S/R \ll S_B/R$, the Brillouin and exact entropy curves run very close together, and the following approximate method of calculating a new $\Delta S/R$ under slightly changed conditions of δ and/or T (say δ_1 , T_1), given a table of exact values for conditions δ_0 , T_0 , is found to be very useful.

Let $\Delta = \delta/2$, $\alpha = \Delta/T$, and $\beta = \mu H/\Delta$. One may then take the expressions for both the Brillouin entropy and the exact entropy and obtain their derivatives with respect to α . Denoting derivatives by a primed symbol, we then have

$$(S_B/R)_\alpha \approx (S_B/R)_{\alpha_0} + (S'_B/R)_{\alpha_0} \times (\alpha - \alpha_0), \quad (\text{Brillouin}) \quad (4)$$

and

$$(S/R)_\alpha \approx (S/R)_{\alpha_0} + (S'/R)_{\alpha_0} \times (\alpha - \alpha_0). \quad (\text{exact}) \quad (5)$$

Subtracting (5) from (4)—for a positive quantity—we find

$$(\Delta S/R)_\alpha = (\Delta S/R)_{\alpha_0} + (\Delta S'/R)_{\alpha_0} \times (\alpha - \alpha_0) \quad (6)$$

to a satisfactory degree of accuracy. It must be emphasized that eq (4) and (5) are only approximate. Higher derivatives have been neglected, but these effectively disappear in the subtraction, which leads to eq (6).

In table 5 the entropy values have been calculated for various values of H , and with $\delta/k=0.27$ deg,

TABLE 4. Entropy as a function of $a (= \mu H/kT)$ calculated from the "Brillouin formula": $S/R = a \coth a - 4a \coth 4a + \log_e \sinh 4a - \log_e \sinh a$

Tables for $J=1/2, 3/2, 5/2, 7/2$ can be found in an article by Hull and Hull [2]; the greater part of table 1 has been taken from this source.

a	S/R	$\log_e 4 - S/R$	a	S/R	$\log_e 4 - S/R$	a	S/R	$\log_e 4 - S/R$
0	1.38629	0	0.40	1.07179	0.3145	1.50	0.20817	1.1781
0.01	1.38604	0.0003	.45	1.00961	.3767	1.55	.19228	1.1940
.02	1.38530	.0010	.50	0.94754	.4387	1.60	.17756	1.2087
.03	1.38405	.0022	.55	.88658	.4997	1.65	.16393	1.2224
.04	1.38231	.0040	.60	.82750	.5588	1.70	.15131	1.2350
.05	1.38007	.0062	.65	.77083	.6155	1.75	.13963	1.2467
.06	1.37735	.0089	.70	.71690	.6694	1.80	.12882	1.2575
.07	1.37415	.0121	.75	.66591	.7204	1.85	.11882	1.2675
.08	1.37047	.0158	.80	.61796	.7683	1.90	.10957	1.2767
.09	1.36632	.0200	.85	.57303	.8133	1.95	.10102	1.2853
.10	1.36171	.0246	.90	.53102	.8553	2.00	.09311	1.2932
.12	1.35115	.0351	.95	.49185	.8944	2.1	.07904	1.3072
.14	1.33887	.0474	1.00	.45543	.9309	2.2	.06705	1.3192
.16	1.32496	.0613	1.05	.42156	.9647	2.3	.05681	1.3295
.18	1.30952	.0768	1.10	.39011	.9962	2.4	.04809	1.3382
.20	1.29266	.0936	1.15	.36091	1.0254	2.5	.04068	1.3456
.22	1.27449	.1118	1.20	.33382	1.0525	2.6	.03438	1.3519
.24	1.25514	.1311	1.25	.30871	1.0776	2.7	.02903	1.3573
.26	1.23471	.1516	1.30	.28543	1.1009	2.8	.02449	1.3618
.28	1.21334	.1730	1.35	.26386	1.1224	2.9	.02064	1.3656
.30	1.19115	.1951	1.40	.24386	1.1424	3.0	.01739	1.3689
.32	1.16824	.2181	1.45	.22534	1.1609			
.34	1.14475	.2415	1.50	.20817	1.1781			
.36	1.12077	.2655						
.38	1.09642	.2899						
.40	1.07179	.3145						

$T=1.1^\circ\text{K}$ (the Brillouin entropy itself is, of course, independent of δ , but the values of H are listed in terms of $\mu H/\Delta$, which appears in the analytical expressions for the exact entropy). We thus have $\Delta=0.135$ and $\alpha_0=0.1227273$. The derivatives are given in columns 3 and 5.

Now, in any experiment, T is determined by experimental conditions, and δ is usually known fairly accurately. (It is not illogical to derive an accurate value of δ from entropy data, the calculation of which involves δ ; it is essentially the method of successive approximation.) These together fix the value of α , and a tabulation of $\Delta S/R$ is readily obtained by making use of table 5 and eq (6).

One then plots a curve of $\Delta S/R$ versus $(S_B/R)_\alpha$ (using eq (4)) to obtain the correction curve appro-

TABLE 5. Brillouin entropy, entropy correction, and first derivatives with respect to α ($=\Delta/T$) for the "standard value" α_0 of 0.1227273 ($=0.135/1.1$), for varying values of β ($=\mu H/\Delta$). $\Delta=\delta/2$ (see text)

$\beta=\mu H/\Delta$	$(S_B/R)_{\alpha_0}$	$-(S'_B/R)_{\alpha_0}$	$(\Delta S/R)_{\alpha_0}$	$(\Delta S'/R)_{\alpha_0}$
0	1.38629	0	0.06747	0.1209
0.4	1.38029	0.097397	.00744	.1197
.8	1.36259	.380323	.00734	.1162
1.2	1.33400	.821912	.00716	.1110
1.9	1.26186	1.856246	.00674	.0983
2.8	1.14042	3.337499	.00605	.0790
3.7	1.00451	4.610410	.00529	.0600
4.6	0.86918	5.478282	.00454	.0435
6.0	.67952	6.036330	.00350	.0238
7.5	.51466	5.909656	.00260	.0097
9.0	.38737	5.417034	.00191	.0010
10.5	.29057	4.787534	.00137	-.0038
12.0	.21734	4.128350	.00093	-.0022

priate to one's own experimental conditions. For any one demagnetization, S_B/R is readily obtained from the H/T value and table 1, and $\Delta S/R$ is read off from the correction curve.

To illustrate the efficiency of the method, table 6 lists values of $\Delta S/R$ calculated rigorously and by the above approximation for the case $\alpha=0.113043$ ($\delta=0.26$ deg, $T=1.15^\circ\text{K}$) and for the case $\alpha=0.133333$ ($\delta=0.28$ deg, $T=1.05^\circ\text{K}$). Inasmuch as one is only interested in an accuracy to the fourth decimal place, or two significant figures, it may be seen that the method is very useful.

TABLE 6. Comparison of entropy-correction values calculated exactly and by the approximate method for the cases (a) $\alpha=0.113043$ ($\delta/k=0.26$ deg, $T=1.15^\circ\text{K}$), and (b) $\alpha=0.133333$ ($\delta/k=0.28$ deg, $T=1.05^\circ\text{K}$)

$\beta=\mu H/\Delta$	$\alpha=0.133333$		$\alpha=0.113043$	
	$\Delta S/R$ (exact)	$\Delta S/R$ (approx.)	$\Delta S/R$ (exact)	$\Delta S/R$ (approx.)
0	0.0088 ₁	0.0087 ₆	0.0063 ₃	0.0063 ₀
3.7	.0059 ₁	.0059 ₂	.0047 ₀	.0047 ₀
10.5	.0013 ₂	.0013 ₃	.0013 ₉	.0014 ₁

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 [2] J. R. Hull and R. A. Hull, *J. Chem. Phys.* **9**, 465 (1941).
 [3] R. P. Hudson, *Phys. Rev.* **88**, 570 (1952).

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