

transition  $M \rightarrow K$  necessitates a quadrupole transition. In an elementary process in which the emitted electron leaves the atom with a kinetic energy  $E$ , we would expect a light-quantum to be emitted with a frequency

$$\nu = \nu_{M_1K} - (1/h)(E + I_\alpha),$$

where  $\nu_{M_1K}$  is the frequency of the  $\beta_5$ -line,  $I_\alpha$  the ionization-energy of the ejected electron. Since  $E$ , beginning with zero, can assume any positive value, the values of this frequency will likewise lie in a continuous range the high frequency limit of which is given by

$$\nu_{\max} = \nu_{M_1K} - I_\alpha/h.$$

We would interpret each step in the intensity-plateau reported above as the beginning of one such continuum, the short wavelength limit being different from electron groups with different ionization energies  $I_\alpha$ . Thus in the case of Mo the continual joining the steps at a wavelength  $\lambda = 627.019$  and  $\lambda = 627.691$  would correspond to the ejection of an  $N_2$  and  $N_1$  electron, respectively. Expressing the difference in frequency from the step to the forbidden line  $\lambda = 625.646$  in units of the Rydberg-frequency, one would thus obtain for the  $N_1$  electron

$$(\nu_{M_1K} - \nu_{\max})_1 = I_{\alpha 1}/h = 4.75 \quad (4.7)$$

and for the  $N_2$ -electron

$$(\nu_{M_1K} - \nu_{\max})_2 = I_{\alpha 2}/h = 3.19. \quad (3.8)$$

These values are in satisfactory agreement with those given in the parentheses and determined from limiting frequencies of x-ray series.<sup>7</sup> It is important to notice that the mechanism here proposed yields also the right order of magnitude for the total intensity of the continuum. Taking only the contribution due to the emission of  $N_2$  electrons, we would expect it<sup>6</sup> to stand to the intensity of the  $K$ -line in a ratio of about

$$6(e^4/E_\alpha^2)(r_i/r_\alpha)^2 \cong 0.2.$$

$E_\alpha$  is the ionization energy of an  $M_3$ -electron, the radii  $r_i$  and  $r_\alpha$  of the  $M_3$ - and  $N_2$ -orbits are estimated from the observed ionization-energies under the assumption of hydrogen-like orbits and the factor 6 is introduced to account for the presence of 6  $N_2$  electrons. Since the intensity of  $K - \gamma$  is about 50 times the intensity of  $K - \beta_5$  this means that the total intensity of the continuum would be about  $50 \times 0.2 = 10$  times stronger than that of the forbidden line. This agrees with the experimental fact that the height of the plateau is approximately the same as that of the forbidden line; its extension however is about 10–20 times bigger.

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April 22, 1935.

<sup>1</sup> Idei, Sci. Rep. Tohoku Imp. Univ. 19, 559 (1930).

<sup>2</sup> Beuthe, Zeits. f. Physik 60, 603 (1930).

<sup>3</sup> Ross, Phys. Rev. 39, 536 (1932); 43, 1036 (1933). Carlsson, Zeits. f. Physik 80, 604 (1933); 84, 119 (1933); Hulubei and Cauchois, Comptes rendus 196, 1294 (1933).

<sup>4</sup> Manning, Rev. Sci. Inst. 5, 316 (1934).

<sup>5</sup> Duane, Proc. Nat. Acad. Sci. 18, 63 (1932).

<sup>6</sup> Bloch. Soon to be published.

<sup>7</sup> Int. Crit. Tables 6, 35 (1929).

### The Thermodynamic Temperature Scale in the Region Below 1° Absolute<sup>1</sup>

In our first experiments<sup>2</sup> on the production of very low temperatures by adiabatic demagnetization Curie's law,  $\chi T = \text{const.}$ , was assumed in obtaining the temperature.

Nearly a year ago experiments to determine true thermodynamic temperatures were performed and since we have not yet found time to report these in detail, we wish to publish a brief account of our results here. The full account will be given later, probably in the *Journal of the American Chemical Society*.

The substance investigated was gadolinium phosphomolybdate,  $\text{Gd}(\text{PMo}_{12}\text{O}_{40})_3 \cdot 30\text{H}_2\text{O}$ . An 89.28 g sample was used for the measurements.

Hoar<sup>3</sup> has shown that this substance is cubic with the gadolinium atoms occupying positions corresponding to those of the diamond type lattice. Thus all gadolinium atoms are equivalent and since there is but one gadolinium in a total of 250 atoms the magnetic atoms are unusually well diluted. This minimizes the interactions which must at sufficiently low temperatures destroy the validity of Curie's law. This law is, in the limiting case, inconsistent with the third law of thermodynamics.

In a paper, soon to appear,<sup>4</sup> we have shown how the application of the first and second laws of thermodynamics to magnetic and calorimetric data will permit the correlation of magnetic susceptibility, field strength and temperature. Here we will mention only the results for the determination of temperature in the special case of zero magnetic field where  $T = de/dS$ .

Magnetic susceptibilities were measured by the inductance coil method.<sup>2</sup> The susceptibility could then be used as a reference in correlating entropy and energy measurements. The entropies were fixed by a series of isentropic demagnetizations which started at known temperatures and magnetic field strengths. This procedure has been described in connection with the determination of the heat capacity of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ .<sup>2</sup>

For fixing the energy it was desirable to avoid the use of the usual electrical connections because of heat leak. We considered many possible sources of heat input such as radiation from a filament, from ordinary temperatures or from a radioactive material, the addition of a small amount of solid of known energy content or the condensation of small amounts of helium gas. Although any of these methods might have been employed we finally decided to use an induction heater. The heater consisted of a closed loop of No. 40 (B. and S. gauge) gold wire about 2 cm in diameter. The gold contained 0.1 percent silver. A small current was induced in the heater by means of a relatively large 60-cycle current in the same solenoid magnet used for the demagnetizing process. Although the total amount of energy introduced for a measurement was about 0.001 calorie it could be determined to the order of about  $10^{-5}$  calorie. The measurements showed that for all temperatures down to 0.30°K the Curie scale for gadolinium phosphomolybdate is within 0.01° of the true thermodynamic scale. However, at 0.25° (Curie) the Curie temperature was 5 percent too low; at 0.20°, 11 percent too

low, and at 0.15° it was 22 percent too low. It should be pointed out that the deviations occur at temperatures where thermal equilibrium is more difficult to attain and that they may possibly be due to this effect. Also it is more difficult to obtain accurate derivatives at the end of the curve. It had been expected that the estimates of temperature on the Curie scale would be too high.

During energy input the temperature of the gold induction heater was considerably above that of the calorimeter but since it had to start operating at the low temperature it was possible to conclude that gold is not a superconductor above 0.15°K. Kurti and Simon<sup>5</sup> have recently found that it is still not a superconductor at 0.05° (Curie-Fe(NH<sub>4</sub>)(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O).

Since the above deviation from Curie's law is in a ferromagnetic direction, measurements were made to detect any permanent magnetism in gadolinium phosphomolybdate. None was found at any temperature to within an accuracy of 1/5000 of the saturation magnetic moment.

Gadolinium nitrobenzene sulfonate, Gd(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>SO<sub>3</sub>)<sub>3</sub>·7H<sub>2</sub>O and gadolinium anthraquinone sulfonate, Gd(C<sub>14</sub>O<sub>2</sub>H<sub>7</sub>SO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O were investigated in terms of their Curie scales. Their properties lie between those of the sulfate and phosphomolybdate as would be expected from the comparative dilution of the magnetic atoms.

All susceptibilities were independent of frequency to 1000 cycles per sec. Possible hysteresis was investigated calorimetrically with a frequency of 550 cycles per sec. Expressed in terms of the energy transferred to the substance at the maximum of the sine wave, approximately 5 parts in 10,000 were converted to heat at 0.15°. At 0.35°, and above, the effect was less than 5 parts in 100,000 which was the limit of accuracy. These figures apply to all of the above salts except the sulfate which was not investigated for hysteresis with 550 cycles/sec. None of the substances showed a detectable hysteresis at a frequency of 60 cycles/sec.

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<sup>1</sup> The results given here were presented at the meeting of the American Chemical Society in affiliation with the American Association for the Advancement of Science, Berkeley, California, June 18-23 (1934).

<sup>2</sup> Giauque and MacDougall, (a) *Phys. Rev.* **43**, 768 (1933); (b) **44**, 235 (1933).

<sup>3</sup> Hoard, *Zeits. f. Kristallographie*, **A84**, 217 (1933).

<sup>4</sup> Giauque and MacDougall, *J. Am. Chem. Soc.*, in press.

<sup>5</sup> Kurti and Simon, *Nature* **135**, 31 (1935).

#### The Ultraviolet Absorption Bands of Diacetylene

The absorption spectrum of diacetylene was investigated with a small Hilger quartz spectrograph, by using an absorption length of about 130 cm. A discrete absorption of about seventy bands was found in the region of  $\lambda\lambda 2900$ – $1900\text{\AA}$ . At a pressure of 1 mm or lower the most intensive bands set in at  $\lambda 2430\text{\AA}$  and extended to the short wavelength limit of the instrument. With increasing pressure, weaker bands in the less refrangible side began to appear

until at a pressure of 250 mm the system extended to  $\lambda 2860\text{\AA}$ ; while in the more refrangible side, the bands broadened to an apparent continuum. Part of the bands are degraded to the red.

The gross structure of the system shows a marked resemblance with the ultraviolet system of dicyanogen.<sup>1</sup> Three distinctive progressions approximately  $2100\text{ cm}^{-1}$  apart can be assigned:

(I) $\nu(\text{cm}^{-1})$	$\Delta\nu$	(II) $\nu(\text{cm}^{-1})$	$\Delta\nu$	(III) $\nu(\text{cm}^{-1})$	$\Delta\nu$
41149 } 43262 } 45353 } 47418 }	2113 2091 2065	41276 } 43409 } 45513 } 47586 }	2133 2104 2073	41521 } 43605 } 45663 }	2084 2058

The bands of these progressions are considered to be due to transitions from the same vibrational level (presumably the vibrationless level) in the ground state to an excited electronic state, (I) with successive excitation of the symmetrical longitudinal vibration ( $\nu' \sim 2100\text{ cm}^{-1}$ ) alone, (II) in addition to the successive longitudinal vibration with one quantum excitation of probably the asymmetrical deformation oscillation ( $\nu' \sim 130\text{ cm}^{-1}$ ), and (III) in addition to the successive longitudinal vibration with one quantum excitation of probably the symmetrical deformation vibration ( $\nu' \sim 370\text{ cm}^{-1}$ ). The resemblance of the structure of diacetylene and dicyanogen has been pointed out by Mecke<sup>2</sup> and his collaborators through an investigation of the infrared and Raman spectra. It is to be pointed out here, that the isosterism between these two compounds is also markedly shown by a comparison of their ultraviolet bands. Because of the complexity of this spectrum, a more detailed investigation with higher dispersion as well as at different temperatures is in progress. A detailed report will appear soon elsewhere.

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<sup>1</sup> S. C. Woo and R. M. Badger, *Phys. Rev.* **39**, 932 (1932).  
<sup>2</sup> R. Mecke, *Eucken-Wolf Hand- und Jahrbuch der Chem. Physik* **9**, II, 392 (1934); B. Timm and R. Mecke, *Zeits. f. Physik* **94**, 1 (1935).

#### The Ultraviolet Absorption Spectrum of ND<sub>3</sub>

I have recently obtained photographs of the absorption spectrum of very pure ND<sub>3</sub>, which was given me by Professor H. S. Taylor of Princeton University. A normal incidence vacuum spectrograph with a 120,000 line 4-inch glass grating, one-meter focus, was used. The spectral region covered was from 2300 to 770 $\text{\AA}$ . Six plates showing eighteen spectra at a variety of pressures of ND<sub>3</sub> were obtained. The spectrograph itself filled with the gas acted as the absorbing column, and so the effect of temperature on the absorption could not be observed.

The most interesting result of this work will be a detailed quantitative comparison of the spectra of NH<sub>3</sub> and ND<sub>3</sub>, in light of the theory of the vibrational isotope