no significant change in *h* with pressure. The bearing of Table VII on further experiment is immediately apparent. Not only does the increased absorption at lower pressures very greatly diminish the accuracy of experiments by decreasing the number of half wave lengths which may be examined, but below 140 mm. the absorption becomes so great that it is likely that Einstein's reasoning would no longer apply. At increased frequencies it seems highly probable that absorption would set in at higher pressures, since Pierce[6] observed at 200 k. c. in carbon dioxide, a similar but non-dissociating gas, an absorption about a hundred times as great as that in air.

Measurements of this character are nevertheless being undertaken by one of us. It seems further advisable to investigate other dissociating gases and vapors in less accessible regions of temperature, for it is by no means certain that the behavior of nitrogen tetroxide is typical of all such dissociation processes.

Summary

1. The velocity of sound at 25° in nitrogen tetroxide has been investigated from 10 to 80 k. c., and from 760 to 140 mm., and has been found to be independent of frequency.

2. It has been calculated that the minimum velocity constant defined by these experiments is not far from the maximum possible velocity constant deduced from the kinetic theory of gases.

3. The bearing of this conclusion on the kinetic theory of reaction velocity is discussed.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

PARAMAGNETISM INDEPENDENT OF THE TEMPERATURE AND THE EXISTENCE OF ELECTRONIC ISOMERS IN POLYATOMIC IONS

BY SIMON FREED AND CHARLES KASPER

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It has been almost universally believed that the phenomenon of paramagnetism owes its origin to the motion of the unbalanced electrons in the stationary states of molecules. Employing the model of such molecular magnets Langevin[1] was very successful in accounting for the magnetic behavior of many substances, not only in the gaseous state where interaction between the molecules is slight, but also in the crystalline state and in solution. He was led to Curie's law, which states that the paramagnetic susceptibility is inversely proportional to the absolute temperature. Many substances, however, display a somewhat more com-

[1] Langevin, *Ann. chim. phys.*, [8] 5, 70 (1905).

plicated behavior and require an arbitrary constant to describe their deviation from Curie's law.[2]

A number of substances have been found to have susceptibility quite independent of the temperature. Their paramagnetic susceptibility is small, usually of the same order of magnitude as the diamagnetic susceptibility. Indeed, such constant susceptibility may well be a general phenomenon experimentally inseparable from the diamagnetic susceptibility, since the latter is also independent of the temperature and in paramagnetic substances it may constitute part of the deviations from Curie's law. Only one type of substance exhibiting constant paramagnetism has been investigated here. It consists of a molecular ion in which a metallic constituent is surrounded with just the number of electrons which suggest a very balanced and symmetrical arrangement. One would, of course, expect such an ion to be diamagnetic. It was the aim in this investigation to observe by precise measurements to what degree the paramagnetism of such ions was independent of the temperature and to correlate their magnetism with the results of the quantum mechanics.

Previous Work and its Relation to the Present Investigation.—Manganese in permanganate ion, MnO_4^-, is in its maximum valence of +7, and it would normally be expected to resemble argon and be diamagnetic, since the latter has all its electrons mutually balanced.[3] Ishiwara[4] measured the specific susceptibility of potassium permanganate over a range of temperatures and found it to be 0.179 at 103°K., 0.175 at 294°K., 0.175 at 368°K. and 0.179 at 435°K.

Similarly, chromium in dichromate ion, $Cr_2O_7^=$, is in its maximum valence of +6. The susceptibility of this ion was found to be constant by Weiss and Collet[5] in solution from 14 to 50° within 1×10^{-6}, and by Collet[6] in the solid state from 12 to 90° to within 0.1×10^{-6}.

There are analogous ions such as UO_2^{++}, $WO_4^=$, VO_3^-, etc., which one would predict to behave similarly.

There is another type of ion manifesting constant paramagnetism,

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[2] A generalized Curie's law known as Weiss' law, $X\ (T + \Delta) = C$, is often obeyed; X is susceptibility, T, absolute temperature. Δ an empirical constant and C is Curie's constant.

[3] Kossel, *Ann. Physik*, **49**, 229 (1916), first observed that the paramagnetic susceptibility of many ions depends only on the number of unbalanced electrons in the valence shell. For example, bivalent vanadium, V^{++}, has three unbalanced electrons and it has three Bohr magnetons (Freed, This Journal, **49**, 2456 (1927)), VO^+ (V^{+++}) has two unbalanced electrons and it has two Bohr magnetons. VO^{++} (V^{++++}) has one unbalanced electron, as potassium has, and it possesses one Bohr magneton. VO_3^- (V^{5+}) has no unbalanced electrons, like argon, and hence would presumably be diamagnetic.

[4] Ishiwara, *Science Reports, Tôhoku Imp. Univ.*, Series I, **3**, 303 (1914).

[5] Weiss and Collet, *Compt. rend.*, **178**, 2146 (1924).

[6] Collet, *ibid.*, **181**, 1057 (1925).

which has some resemblance to the ions just mentioned, namely, the cobaltammines[6] and similar complex ions, and the ferrocyanide ion. The number of electrons surrounding cobalt in the cobaltammines is 36. The same number surrounds iron in ferrocyanide ion. Argon has the same number of electrons[7] and these, of course, balance completely and form a diamagnetic system.

Experimental Method

It was found that the method of Freed[8] for measuring susceptibilities at low temperatures would justify the use of a more sensitive balance than the one he employed. In the present work the apparatus was equipped with a Sartorius micro-balance having a capacity of 20 g. and a sensitivity under ideal conditions of ±0.001 mg. Under the conditions of the experimentation a sensitivity of about ±0.007 mg. was reached but the reproducibility was reduced to ±0.01 mg. or ±0.02 mg. by the fluctuations in the current exciting the magnet.

In short, the method consists in employing the use of the Gouy method at low temperatures in such a way that the tube containing the substance to be measured is in a regular stream of hydrogen at known temperatures. The hydrogen is cooled by liquid air, for example, boiling under atmospheric pressure, or to obtain lower temperatures, under reduced pressure. The stream of hydrogen gas is not connected with the vacuum pump and the tube swings just as freely at all temperatures as if it were suspended in air under atmospheric pressure. The balance can thus be manipulated as under normal conditions.

Materials and Experimental Results.—The chemical substances which were utilized in this work were analyzed for iron by the sensitive thiocyanate method and also for any other paramagnetic impurities that were likely to be present. Most careful attention was given to the possible presence of the metals of the ions in less than their maximum valence, for example U^{4+} in UO_2^{++}, Cr^{+++} in $Cr_2O_7^{=}$, etc. These are all paramagnetic and their undetected presence in appreciable concentration would have been disastrous. For this purpose, we observed colorimetrically the effect of adding permanganate solution drop by drop. This procedure was impossible in the case of dichromate due to its intense color. To avoid this, recrystallized potassium dichromate of great purity was measured magnetically and its susceptibility was found to increase slightly as the temperature was reduced. The same material was then recrystallized in the *cold*, that is by pumping off the water from a saturated solution at room temperature and distilling it into a liquid–air trap. The resulting dichromate crystals showed no temperature coefficient in the

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[7] Welo and Baudisch, *Nature*, 116, 606 (1925).

[8] Freed, THIS JOURNAL, **52**, 2702 (1930).

susceptibility. Perhaps it may be stated that the original paramagnetic contamination was so small that it would not have been detected by the previous investigators.

The susceptibility of uranyl ion decreased at first as the temperature was lowered, but increased again at lower temperatures. However, when the presence of iron was corrected for, the susceptibility continued to decrease steadily. If other undetected paramagnetic impurities had been present, the true susceptibility of UO_2^{++} would be decreasing more rapidly with decreasing temperature than appeared to be the case.

The sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, was exceptionally free of impurities. It was recrystallized once.

The computation of the partial molal susceptibilities was made by assuming that the susceptibilities of the constituents were additive.

TABLE I

THE SUSCEPTIBILITIES OF UO_2^{++}

Temp., °K.	$X^{a}_{\text{gr. } UO_2SO_4 \cdot 3H_2O}$	$X^{b}_{\text{mole } UO_2^{++}}$
293.2	−0.0232	57.03
116.3	− .0212	56.28
90.8	− .0203	55.98
69.8	− .0228	53.97

[a] *Uncorrected for ferric ion present.* [b] Corrected for iron (2×10^{-6} g. per g. salt).

The second column is the susceptibility per gram of the salt $UO_2SO_4 \cdot 3H_2O$, which is effectually the difference between the susceptibilities of the paramagnetic and diamagnetic constituents. The partial molal susceptibility of UO_2^{++} can be ascertained with a greater percentage accuracy than this difference is known, provided the magnitudes of the diamagnetic susceptibilities are assumed to be without appreciable error. Such an assumption is justified, perhaps, in the case of liquid water. (The susceptibility of ice is a trifle less but is not known with the same accuracy.) 12.96×10^{-6} per mole was taken as its susceptibility. However, the molal susceptibility of $SO_4^{=}$ is only very approximate and should be redetermined. The value of -37.00×10^{-6} per mole was arbitrarily adopted for it. This value is correct to within about 3%. We cannot then insist upon the absolute magnitudes in the third column. The variation with the temperature is known with far greater accuracy than the values of the susceptibilities themselves. It was, of course, these variations with which this research was primarily concerned. The reproducibility in the measurements was such that a change in the susceptibility per gram of 0.0005×10^{-6} could be definitely established. Such a sensitivity corresponds to a change of 0.06×10^{-6} per mole.

Greater precision than this in terms of actual effects on the balance was obtained in the measurements of sodium tungstate. However, the pull was so great, about 10 mg. (it was only from 0.8 mg. to 1.7 mg. with $UO_2SO_4 \cdot 3H_2O$), that slight fluctuations in the current brought the reproducibility to ±0.02 mg. The susceptibility was measured at 296.5°K., 115.2°K. and 86.4°K. and was found to be constant. Of a total of thirty-six points only two deviated from the smooth curve of pulls against amperes by 0.03 mg. and one by 0.04 mg. The susceptibility per gram of the salt was found to be -0.1958×10^{-6} and the *susceptibility per mole of* $WO_4^{=}$ becomes $+5.93 \times 10^{-6}$. A change of 0.0005×10^{-6} per gram or 0.08×10^{-6} per mole would have been observed easily. The value of -10.4×10^{-6} was taken as the susceptibility of one mole of Na^+.[9]

Finer reproducibility was attained with $Cr_2O_7^{=}$. The purified potassium dichromate was measured at 293.6°K., 169.9°K., 114.0°K. and 84.3°K. and found to be constant. The measured values fell upon a smooth curve within ±0.01 mg. Of the thirty-six points only one deviated by more than this, and it deviated by 0.03 mg.

Another series of determinations was made to obtain the absolute susceptibility. It was suspected that the balance might have been jarred slightly since the previous calibration had been made. However, this series agreed with the first within 0.02 mg. The susceptibility per gram was found to be $+0.0962 \times 10^{-6}$. Employing the value of -16.9×10^{-6} as the molal susceptibility of K^+[9], the *susceptibility of one mole of* $Cr_2O_7^{=}$ *is* 62.1×10^{-6}. A change of 0.1×10^{-6} per mole would have been observable.

Discussion of Results

The existence of fluorescence from uranyl ion, UO_2^{++}, shows clearly the existence of an unusual freedom from interaction with external systems. Otherwise, the high density of matter in thermal agitation in the crystal would have quenched the fluorescence. The independence of the dichromate ions from one another is further confirmed in the identical susceptibility which dichromate ion has in solution and in the solid state. In the same way, the sharpness of the absorption bands of the permanganate ion, MnO_4^-,[10] indicates that its least stable electrons, that is, those to which one may assign the optical and paramagnetic properties of MnO_4^-, are shielded from external forces.

To a considerable degree of approximation, then, the least stable electrons of the ions we have been discussing may be regarded as localized near the metallic kernel of the ion and shielded from the external fields of the neighboring ions by the atmosphere of electronically saturated oxygen atoms (or ammonia, etc., in the cobaltammines or cyanide in the cyanides, etc.). Such a configuration immediately suggests the atomic

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[9] Ikenmeyer, *Ann. Physik,* [5] 1, 169 (1929).

[10] Hagenbach and Percy, *Helv. Chim. Acta,* 5, 454 (1922).

ions of the rare earths whose kernels contain the unbalanced electrons. These, too, are shielded from external forces by electronically saturated shells, that is, by electronic shells which are completely filled.

The ions of the rare earths conform very closely in their magnetic behavior[11,8] with that expected from independent ions. Indeed, their magnetic susceptibilities can be calculated accurately from considerations employed in the quantum theory of atoms (atomic ions.) Correspondingly we shall attempt to correlate the magnetic properties of the molecular ions, such as UO_2^{++}, $WO_4^{=}$, $Cr_2O_7^{=}$, MnO_4^{-}, etc., with the quantum theory of molecules.

Van Vleck[12] in a series of important papers on susceptibility from the point of view of the quantum mechanics arrived at the following formula

$$\chi = \frac{N}{3kT}\frac{\Sigma_{\sigma jm,\, j'm'}\,|\,M(\sigma jm;\ \sigma j'm')\,|^2\, e^{-W(\sigma j)/kT}}{\Sigma_{\sigma jm}\, e^{-W(\sigma j)/kT}} \tag{1}$$

$$+ \frac{2N}{3h}\frac{\Sigma_{\sigma jm,\, \sigma'j'm'\ (\sigma \neq \sigma')}\,\dfrac{|\,M(\sigma jm;\ \sigma'j'm')\,|^2}{\nu(\sigma;\ \sigma')}\, e^{-W(\sigma j)/kT}}{\Sigma_{\sigma jm}\, e^{-W(\sigma j)/kT}} \tag{2}$$

$$- \frac{Ne^2}{6mc^2}\Sigma r^2 \tag{3}$$

where χ is the susceptibility per mole, k is Boltzmann's constant, T is the absolute temperature, σjm are indices or quantum numbers of the molecule in a stationary energy state, σ is an index corresponding to quantum numbers whose change is associated with an energy W (σ), large compared with kT (in the present case we may identify it with electronic quantum numbers), j corresponds to quantum numbers whose change implies energies small compared to kT (in this case the rotational quantum number, m, corresponds to quantum numbers whose change is associated with energies small compared with kT, in this case, magnetic quantum numbers), ν (σ; σ') is the absorption frequency corresponding to a transition from the state σ to σ' (it is practically equal to ν (σjm; $j'm'$—, since the change in σ is associated with a greater energy difference than is brought about by the change in the other quantum numbers), e/m is the charge divided by the mass of the electron, N is Avogadro's number, h is Planck's constant, c is the velocity of light and Σr^2 is the average of the square of the radii of the electronic orbits summed over all the electrons.

$|\,M(\sigma jm;\ \sigma j'm')\,|^2$ is the square of the absolute magnitude of the magnetic moment generated by the electrons in the stationary electronic state of the molecule. (If the molecule is symmetrical as one would believe MnO_4^{-}, UO_2^{++} to be, an axis of symmetry exists with respect to which the angular momentum of the system may be resolved. $\Sigma j'm\ |\ M(\sigma jm;$

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[11] Hund, *Z. Physik*, **33**, 855 (1926).

[12] Van Vleck, (a) *Phys. Rev.*, **29**, 727 (1927); (b) **30**, 31 (1927); (c) **31**, 587 (1928).

$\sigma j'm') \mid^2$ can be visualized as the square of the magnetic moment parallel to this axis and $\Sigma \sigma j'm'(\sigma \neq \sigma') \mid M(\sigma jm;\ \sigma' j'm') \mid^2$ as the square of the magnetic moment perpendicular to this axis.) $\Sigma \sigma' j'm'(\sigma \neq \sigma') \mid M(\sigma jm;\ \sigma' j'm') \mid^2$ is the square of a sort of average magnetic moment associated with the transition $\nu(\sigma;\ \sigma')$.

$M(\sigma jm;\ \sigma' j'm')$ can be identified according to Van Vleck[13] and others as resulting from the fluctuation in angular momentum between the nuclei and the electrons. On the average the angular momentum in a stationary state of such ions as UO_2^{++} and $WO_4^{=}$ (doubtless having $^1\Sigma$ levels for their basic electronic states) is zero but instantaneously the square of the angular momentum (or magnetic moment) is not zero. The susceptibility arising from the magnetic moments of the stationary states would naturally be affected by the thermal agitation which counteracts the alignment induced by the magnetic field. Hence its susceptibility would show a dependence upon the temperature. The moment associated with a fluctuation which occurs with the frequency $\nu(\sigma;\ \sigma')$, which is very rapid as compared with thermal collisions, would of course not reflect its effect on the susceptibility as a function of the temperature. In line (2) we do not find T as a factor in the denominator. The Boltzmann factor contains the temperature, but its influence is inappreciable when the frequency is high. This term then becomes practically a constant. In fact, Van Vleck shows that when energy changes associated with j and m are small compared to energy changes associated with σ, then form (2) reduces to

$$\frac{2N}{3h}\Sigma \sigma(\sigma \neq \sigma') \frac{\mid M(\sigma;\ \sigma') \mid^2}{\nu(\sigma;\ \sigma')} \tag{2a}$$

which is independent of the temperature. Line (3) comprises the diamagnetic contributions to the susceptibility. This results, of course, from the moment induced by the magnetic field and is not present in its absence.

As we have observed in the introduction, the ions we have been discussing have their net electronic moments equal to zero and hence would normally be diamagnetic. The first term in the summation on line (1) is then zero. Since the measured susceptibilities are practically independent of the temperature, the other terms of this summation are small, not because the moments in the activated states are zero (such a possibility is only very slight), but because the number present in those states is small. This number is, of course, regulated by the Boltzmann factor, which is small when the energy of activation, the frequency of transition, is large. The form of the term shows that the contribution of these activated molecules to the susceptibility would tend to have but a small temperature coefficient over a restricted temperature range. For example, the number present in the activated states increases with the tem-

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[13] Ref. 12c, p. 606.

perature, but on the other hand their susceptibility decreases. The bulk of the constant susceptibility arises from the second line, the so-called fluctuation term.

Since neither the frequency of transition in these ions nor the magnetic moments in their activated states are yet known, we must speak only in more or less qualitative terms. The results show that UO_2^{++} becomes less paramagnetic as the temperature is reduced (any paramagnetic impurity would introduce an opposite trend). The small variation over so considerable a temperature range indicates that the fluctuation term is the predominant one, that the electronic frequency probably lies in the infra-red and that the number in the activated level increases more than linearly with the temperature.

The constancy in the paramagnetism of $WO_4^{=}$ implies that the frequency of transition to the first electronic level (possessing a magnetic moment) is probably higher than that of UO_2^{++}. It follows that the contribution of the "parallel" (or temperature) component is small and also that the fluctuation term is small since the same high frequency occurs in its denominator. The actual magnitude of the susceptibility of $WO_4^{=}$ is really small. $WO_4^{=}$ is colorless and it is conceivable that the first electronic activation lies in the ultraviolet. Indeed, it may possibly lie in the continuum of dissociation.

$Cr_2O_7^{=}$ also possesses a paramagnetism independent of the temperature. The same reasoning applies to dichromate as to tungstate. If the first electronic activation corresponds to light in the visible, the frequency would be more than high enough to account for the lack of a temperature coefficient in its susceptibility.

MnO_4^- measured by Ishiwara[4] is the only ion of this type other than UO_2^{++} whose susceptibility is known to decrease with the temperature. At the lowest temperature, however, he found it to increase again. This is exactly the same behavior that UO_2^{++} apparently followed before its susceptibility was corrected for the presence of ferric ion. It appears very probable indeed that Ishiwara's potassium permanganate was slightly decomposed (by light, perhaps, or by some contact with organic matter, to which potassium permanganate is extremely sensitive), and as a result the paramagnetic manganese dioxide is present. Even a minute contamination becomes significant at the lower temperatures as its susceptibility is constantly increasing. If this slight impurity be discounted, the conclusion is reached that the susceptibility of MnO_4^- decreases steadily with the temperature just as UO_2^{++} was found to do, and the influences discussed in the case of UO_2^{++} apply here also.

In this discussion it has been assumed that the frequency $\nu(\sigma;\ \sigma')$ in the denominator of the fluctuation term does not vary with the temperature. This constancy is definitely not fulfilled in solids, as variations have been observed in the line spectra of the rare earths.[14] However, the magnitude of the change is small. The fact that both $WO_4^=$ and $Cr_2O_7^=$ display a susceptibility independent of the temperature indicates that the influence in ions of this nature is inappreciable.

Summary

The degree of dependence of the susceptibilities of UO_2^{++}, $WO_4^=$ and $Cr_2O_7^=$ on the temperature has been accurately studied from room temperature to that of liquid air.

The susceptibility of UO_2^{++} was found to decrease slightly and uniformly as the temperature was reduced. It is pointed out from the work of Ishiwara[4] that MnO_4^- behaves very probably in the same way.

$WO_4^=$ and $Cr_2O_7^=$ showed no variation in their susceptibilities within the experimental error. The latter ranged from 0.06×10^{-6} to 0.1×10^{-6} per mole or about 0.0005×10^{-6} per gram.

Various properties of these ions are taken as evidence that the ions are of such a nature as to permit the application of the modern theories of magnetism.

The constant paramagnetism of these ions[15] is related to the results of Van Vleck derived from the quantum mechanics. As a consequence, the existence of electronic isomers in these molecular (polyatomic) ions is recognized.

From this point of view, constant paramagnetism is a general phenomenon and is associated with the existence of activated electronic energy levels in molecules (or their ions) in the solid state and in solution as well as in the gaseous state.

BERKELEY, CALIFORNIA

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[14] Freed and Spedding, *Phys. Rev.*, **34**, 945 (1929).

[15] It is very probable that the constant paramagnetism exhibited by some solids cannot be approached in this manner. Their molecules cannot be regarded as isolated with sufficient approximation, and interactions characteristic of the crystal come into play. Magnetic oxides like CuO probably would be in this category. One would scarcely expect their partial molal susceptibility in solution in some diamagnetic medium to have the same value as in the pure solid. Such an identity in the susceptibilities actually exists among the ions we are studying. The constant paramagnetism exhibited by metals seems to have found a satisfactory explanation on the assumption of an electron gas in the metal obeying the Fermi–Dirac statistics; Pauli, *Z. Physik*, 41, 81 (1927).