thermal dissociation of gases, e.g., $O + O = O_2$ + heat, the densities or pressures would become simply expresssed in terms of concentrations and w would have to change sign at that degree of dissociation for which $\rho = \rho_0$ (density of O = density of O_2) without any obvious physico-chemical significance thereto.

With such considerations in mind I have been in the habit of saying that the Boltzmann equation $\rho = \rho_0 \exp(-w/kt)$ was no statistical or thermo-dynamic theorem of universal applicability and that in every case where it is used care should be taken to prove its availability or to specify the significance of w as work done or to emphasize the entirely tentative nature of its use. It was with this viewpoint that I spoke perhaps slightingly of the equation in my paper on metallic conduction in these PROCEEDINGS (9, p. 137, 1923; see also, E. H. Hall, *Ibid.*, 11, p. 36, 1925) and I should not now be reverting to the matter had not persons in whose judgment I have confidence expressed the opinion that there is still enough confusion in the matter to make this note of service. It may be pointed out that if V be the potential energy of the external field and ϵ the intrinsic energy of the gas so that the complete heat function χ is $\epsilon + pv + V$, then we may show that $\Delta\chi = t \int (\partial p/\partial t)_v dv$ which in the case of van der Waal's equation leads to the relation per molecule.

$$(\Delta\chi) \text{ per molecule} = kt \log[(v-b)/(v_0-b)] \quad \text{not} \quad kt \log(v/v_0);$$

and if we choose to take $w = (\Delta\chi)_{p. m.}$, we have a simple result in terms of the covolumes, though not simple in densities unless one wishes to measure density in terms of the volume unoccupied by molecules.

THE BAND SPECTRA OF CRYSTALS AND COMPLEX GASES

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The luminescent spectra of the uranyl salt crystals first discussed from the modern standpoint by Ehrenfest presents some radiation characteristics of a remarkable nature. These crystals at liquid-air temperatures as discovered by J. Becquerel and Onnes in 1903 have a large number of narrow bands occurring at definite intervals across the invisible spectrum. The experimental results of E. L. Nichols[1] and associates for the simplest cases of frequency arrangement we put in the following form. The spectrum consists of high frequency and low frequency branches, the two sets of branches having different spacing constants. For the high frequency

side (absorption) the interval is in round numbers, 700 units for a given series of bands

$$\nu = k + a_1 n_1 + \ldots \quad (1a)$$

and for the low frequency side (emission) the interval is 850,

$$\nu = k - a_2 n_2 + \ldots \quad (1b)$$

In addition there are several series of bands of slightly different constant interval. The complete spectrum involves an equation of the well-known band spectral type

$$\nu = k + (a_1' n_1' - a_1'' n_1'') + (a_2' n_2' - a_2'' n_2'') + \ldots + (b_1' n_1'^2 - b_1'' n_1''^2).$$
$$+ (b_2' n_2'^2 - b_2'' n_2''^2). \quad (1c)$$

An important series of closely related investigations by Schaefer[2] has shown that the near infra-red bands of a large number of crystals are due to localized vibrations of definite atoms. Nichols found that in solutions the character of the spectrum was changed somewhat which we interpret as the effect of coupling upon the characteristic localized vibrations, due to the solvent molecules.

This evidence makes it unnecessary to consider the remark of Bohr, Kramers and Slater[3] that in macroscopic phenomena wherein the entire body takes part in the vibrations that the original conception of stationary states loses its meaning.

It has been demonstrated by Heurlinger, Kratzer,[4] Hulthen,[5] Runge and others that in many cases the different quantum transitions have a common initial or end state. Under these conditions the formula requires one less constant. Thus equation (1c) becomes on putting a_1'' equal to a constant, say zero

$$\nu = k + a_1' n_1' + + \ldots, \quad \text{with spacing } a_1'. \quad (1a')$$

(We are here concerned with the assumption that the transitions to or from certain stationary states are sufficiently characteristic to be identified On putting a_1' equal to a constant there results

$$\nu = k - a_1'' n_1'' + \ldots, \quad \text{with spacing } a_1''. \quad (1b')$$

The difference between the spacings in the two branches of the uranyl spectra is thus the difference between a_1' and a_1''.

That this effect is general and is independent of a constant interval can be seen by an example $B^{11} 0.$[6]

A related example is the investigation of T. Tanaka[7] showing the change in frequency interval of successive bands with change in atomic weight of the active metal in the spectra of solid solutions. The spectra seem to be of the same type as those of the uranyl salts dissolved in glass or fluxes. There are for each active metal in a solid solution equations of type 1a.

TABLE I

n_1'	n_1''	ν	DIFF.	n_1'	n_1''	ν	DIFF.
5	0	48975.3		0	0	42889.8	
			1178.8				1860.9
4	0	47796.5		0	1	41019.9	
			1199.3				1837.5
3	0	46597.2		0	2	39182.4	
			1218.2				1814.0
2	0	45379.0		0	3	37368.4	
			1237.9				1790.4
1	0	44141.1		0	4	35578.0	
			1260.3				1764.7
0	0	42880.8		0	5	33813.3	

The longest series have as many successive bands as 39, over the whole range the interval being constant within the experimental error. This unusual combination of equally spaced bands indicating harmonic motion and large quantic transitions indicating non-harmonic motion may be satisfactorily solved in the following way. The motion in the initial stationary state contains higher harmonics leading to large transitions. The motion in the final state is simple harmonic containing insignificant quadratic terms and leads to equally spaced bands. This may be clearly illustrated by Henri's[8] data on the ultra-violet absorption of benzene.

TABLE 2

n_2	$n_1 = 0$		DIFF.	$n_1 = 2$		DIFF.
	CALC.	OBS.		CALC.	OBS.	
0	37494	37494		37168	37172	
			924			921
1	38415	38418		38089	38093	
			917			
2	39337	39335				
			924			
3	49258	49259		39932	39933	
			921			921
4	41179	41178		49854	40854	
			924			920
5	42101	42102		41775	41774	
			920			919
6	43022	43022		42696	42693	
			916			
7	43944	43938				

The calculated values are given by the formula

$$\nu = 37{,}494 + 921.4\, n_2 - 159\, n_1 - 2\, n_1^2 \tag{2}$$

where n_1 refers to the initial state and n_2 refers to the final state.

In the data of Tanaka not only is there a continuous relation between the nuclear frequencies of all the metals but the absolute frequency range is so nearly the same for the strongest and best spectra that there must be

a common physical constituent in all the vibrating systems. The series electron orbit we consider as approximately fixed with respect to this constituent. Under these circumstances let the mass of the metal atom be M, the mass of the atoms vibrating with it p and let the mass of the oppositely vibrating constituent be q. Then so far as dependence on mass is concerned since $1/\mu = (1/[M + p]) + 1/q$ and $\nu \sim \sqrt{1/\mu}$ we see that the frequency should vary as $\sqrt{(1/[M + p]) + 1/q}$. For all values of p and q, however, this radical when plotted against M lies well above Tanaka's curve. Hence as would be expected the complications of the unknown ionic radii and crystalline coupling forces must be taken into consideration to get a closer approximation to the experimental curve.

Finally we may remark upon the meaning of the linear terms in equation 1c. Henri[9] and associates have found in the case of several organic vapors that the spectra must be expressed by the use of multiple linear terms. These spectra appear to be more general applications of simultaneous combination transitions used by Hettner in explaining infra-red oscillation bands for which no electron transition occurred. In line spectra this has been discussed by Wentzel, Saunders and Russel, Epstein and others.[10] In the gases studied by Hettner[11] the coefficients a were always of the same sign from which he concluded that the quantic numbers must all increase or all decrease. This rule does not hold when applied to the visible spectra of Henri, however.

The visible spectra gives a better insight into the phenomenon of multiple transitions because we may in some cases gain information about the nuclear quantum levels. Referring to the benzene data (equation 2) we see that one fundamental frequency is connected with the initial state corresponding in 1c to $a_1' \, n_1'$ while the other fundamental connected with the end state corresponds to $a_2'' \, n_2''$.

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