

It is possible to write an explicit formula for the final Q , but this does not seem desirable. By working out the power series, step by step, it is much easier to cut off the expansions at the right point.

The occurrence of several oscillations, with both anharmonic and coupling terms, causes no difficulty. Thus, for the energy

$$\epsilon = \omega_1 u(1 - xu) + \omega_2 v(1 - zv) - yuv$$

we have, using only the first two terms of the expansion,

$$Q = \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} s^u t^v (1 + au^2 + buv + cv^2) \\ = ST + as(1+s)S^3T + bstS^3T^2 + ct(1+t)ST^3,$$

where

$$s = e^{-h\omega_1/kT} \quad S = 1/(1-s), \\ t = e^{-h\omega_2/kT} \quad T = 1/(1-t), \\ a = h x \omega_1 / kT \quad b = h y / kT \quad c = h z \omega_2 / kT.$$

If the frequency ω_2 is doubly degenerate, a factor $(v+1)$ is introduced before summing. It may happen in such a case that the anharmonic term involves the azimuthal quantum number l . This causes no trouble, since a preliminary summation over l , by using such formulas as

$$\sum_{l=0}^v l = v(v+1)/2, \\ \sum_{l=0}^v l^2 = v(v+1)(2v+1)/6,$$

Light Excitation in Neon by Lithium Ions

In view of the recent experiments of Beeck¹ and Beeck and Mouzon^{2, 3} on the threshold values for ionization of the noble gases by alkali ions, it was thought worth attempting to observe directly the potential at which light excitation occurs. Since Güntherschulze and Keller⁴ have found neon to be more strongly excited than other gases in low potential discharges, we have tried Li^+ on Ne for which Beeck and Mouzon determined an ionization potential of 307 volts.

The lithium ions were produced by a heated platinum filament coated with spodumene as described by Bainbridge.⁵ The ions were accelerated through a distance of 3 mm by potentials ranging from 150 to 550 volts. The beam was collimated by a hole, 6 mm in diameter and 10 mm long, the end of which was covered by a fine nickel gauze. Upon leaving the collimating slit, the ions entered a field free observation chamber 1.7 cm long at the end of which was a large cylindrical collector connected to a galvanometer to measure the ion current. The parts of the tube exposed to light from the filament were coated with a carbon deposit to prevent scattering.

The gas pressure was so regulated that no discharge appeared when the accelerating potential was applied to the tube with the filament on or off. This procedure prevented a beam of Ne^+ ions entering the observation space. The neon used had no spectroscopic impurities.

The light intensity of the beam of Li^+ ions in Ne was

will always give a power series in v .

It is not necessary to give detailed formulas for the various possible cases; the method is sufficiently flexible so that it may be applied to almost any situation which will be met in practice, with a considerable saving in computation. It is clear, of course, that the temperature derivatives of Q may also be obtained in this way.

The accuracy of the results is limited almost entirely by the number of terms used in the expansions; the only unavoidable error is that of replacing the sum over rotational terms by an integral; this error does not affect the leading term in the expansion, and makes but a slight difference in the other terms. The unavoidable error in Q , will certainly be less than 0.01, which would be less than one part in 10^5 for most applications; to calculate the entropy to 0.001, the accuracy needed in Q is only one part in 2000.

This method has been applied to check various calculations in the literature, with excellent results. It will be used also in a forthcoming work from this laboratory dealing with the entropy and free energy of nitrous oxide.

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compared photometrically with the light from a 10 watt lamp appropriately screened to reduce the light intensity and to obtain an approximate color match. While no photometric settings could be made below 200 volts, the light from the beam could be detected as low as 160 volts. Before these measurements were taken the observer sensitized his eyes for faint light by remaining in total darkness for 15 minutes.

That the light of the beam was due to excitation of Ne rather than of the Li^+ was determined by replacing the collector cup by a flat plate and applying a retarding field for the ions in the observation space. The length of the luminous beam decreased in a regular manner with the increase of retarding potential. It was found that the luminous beam stopped short of the retarding plate while the field was still low enough to permit the ions to reach the plate.

Secondary electrons produced at the collimating slit by

¹ O. Beeck, Ann. d. Physik **6**, 1001 (1930).

² O. Beeck and J. C. Mouzon, Ann. d. Physik **11**, 737 (1931).

³ O. Beeck and J. C. Mouzon, Ann. d. Physik **11**, 858 (1931).

⁴ A. Güntherschulze and F. Keller, Zeits. f. Physik **72**, 143 (1931).

⁵ K. T. Bainbridge, J. Frank. Inst. **212**, 317 (1931).

the impact of Li^+ ions had no effect upon the measurements since their measured velocity was too small to produce excitation in Ne. The results were the same no matter whether the potential of the collector was the same as, slightly greater, or slightly less than the plate containing the collimating slit.

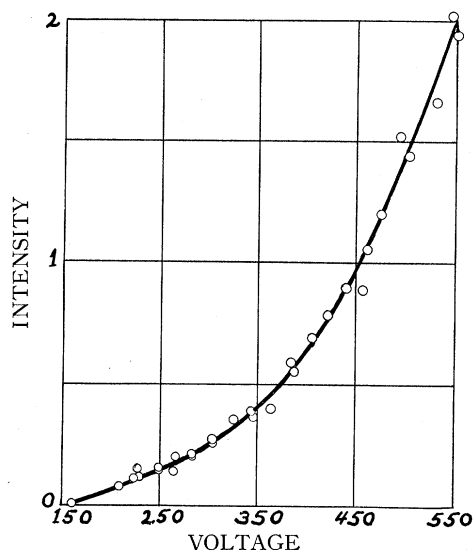


FIG. 1.

The curve shown in Fig. 1 is a composite of four sets of readings. The curves were adjusted by fitting the 386 volt point. The light intensity zero indicates the minimum light intensity observable.

It is interesting to note that light excitation by the Li^+ ions in Ne can be observed approximately 150 volts below the potential at which Beeck and Mouzon observed the beginning of ionization. The curve showing the variation of light intensity with voltage approaches the axis in an asymptotic fashion, whereas Beeck and Mouzon's ionization curve approaches the axis sharply. The fact that Beeck and Mouzon observed a sharp onset of ionization may be due to the fact that the accuracy of their method is limited by the sensitivity of the electrometer for collecting the ion current. In their apparatus the appearance of negative current was observed and taken to indicate the ionization of the gas. However, photoelectrons set free by the radiation excited may have been present at much lower voltages.

These measurements on excitation of light by alkali ions in the noble gases are being extended and a more complete report will be published in the near future.

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The Plasticity of Rocksalt and Its Dependence upon Water

In a letter with the same title Mr. Bowling Barnes communicates the fact that rocksalt crystals after being soaked in water and then dried on the surface, show infrared absorption which depends on the water soaked into the crystal.¹ The suggestion that the entrance of water into the rocksalt crystals is possible and, moreover, may be connected with the high plasticity of "wet" rocksalt, first was introduced by me² and not by Polanyi and Ewald, as Barnes incorrectly states. In collaboration with Quittner, moreover, I have shown that the electric conductivity of rocksalt increases by soaking and subsequent drying of the surface. By this fact an indirect proof of the entrance of water into the crystal was given.³ The direct spectroscopic finding of water in the crystal by Barnes is a most satisfactory proof and an essential completion of our former results. It will be of great interest to measure the quantity of water per cc by the method of Barnes.

Whether the high plasticity of wet rocksalt can find sufficient explanation by these results, I, nevertheless, regard as uncertain.

The opinion of Joffé that the high tensile strength of wet crystals is induced by healing of the fissures of surface without any assistance of plasticity, we have disproved by experiment,⁴ as well as the suggestion of Polanyi and Ewald that watering effects a reduction of the elasticity limit below the tensile strength of dry rocksalt. In fact, dry rocksalt has a limit of elasticity less than the tensile

strength,⁵ agreeing quantitatively with the limit of elasticity for wet rocksalt.⁶

Experiments on the rupture of dry rocksalt crystals⁷ as well as on the dependence of tensile strength on temperature⁸ indicate that rupture starts from surface fissures generated by plastic deformation. By levelling the surface of crystals such disturbances may be eliminated, with the result that rupture occurs only at markedly higher tensile stresses. Moreover, it must be remembered that the high tensile strength of wet rocksalt has been proved only for very small cross sections. If the translation planes in the case of small cross sections effect less significant surface

¹ R. B. Barnes, *Phys. Rev.* **43**, 82 (1933).

² A. Smekal, *Naturwiss.* **16**, 743, 1045 (1928); *Phys. Zeits.* **32**, 187 (1931).

³ F. Quittner and A. Smekal, *Zeits. f. physik. Chemie* **B3**, 162 (1929); *Phys. Zeits.* **32**, 187 (1931).

⁴ A. Smekal, *Phys. Zeits.* **32**, 187 (1931); U. Heine, *Zeits. f. Physik* **68**, 591 (1931).

⁵ A. Smekal, *Phys. Zeits.* **31**, 229 (1930); F. Blank, *Zeits. f. Physik* **61**, 727 (1930).

⁶ K. H. Dommerich, *Zeits. f. Physik* **80**, 242 (1933); G. F. Sperling, *Zeits. f. Physik* **74**, 476 (1932).

⁷ A. Edner, *Zeits. f. Physik* **73**, 623 (1932). H. Schönfeld, *Zeits. f. Physik* **75**, 442 (1932).

⁸ W. Burgsmüller, *Zeits. f. Physik* **80**, xxx (1933).