$(1\bar{2}10)$ plane of the crystal. As is well known,[2, 3] the pattern obtained from the nonoscillating plate showed double lines. Oscillating the sample by an ordinary Pierce circuit in its first harmonic (cycle $=4.5\times10^5$), the component lines of each doublet are enhanced and widened towards each other as is seen in Fig. 1, which leave between them a weak region which corresponds to the median nodal plane of vibration. Fig. 2 gives the pattern when oscillated in its third harmonic. Here we see that, besides the general increase of the reflection from the interior part of crystal, the doublets are replaced by four lines corresponding to four planes of loop of the third harmonic.

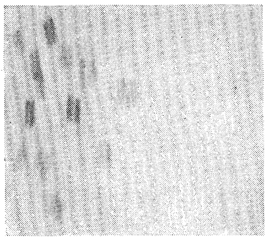

FIG. 1.

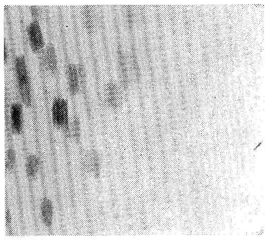

FIG. 2.

If the shearing motion takes place only in the direction of electric axis, we could expect the increase of the intensity of x-ray reflection very great for such net planes as $(1\bar{2}10)$, but relatively small for ones as $(\bar{1}011)$. To test this point a spectrometric measurement was made by transmitting Mo $K\alpha$ radiation through a similar R-cut plate, $0.258\times3.1\times3.2$ cm^3. The result was as just expected, *viz.*, the reflection from the net plane $(\bar{1}011)$ was found to suffer little effect while that of the $(1\bar{2}10)$ plane to show a large increase of intensity by the vibration. In the latter case, the intensity under oscillation with the plate voltage of 396 volts in the exciting circuit, was about four times, for the fundamental (cycle $=9.5\times10^5$), and about twelve times, for the third harmonic, that observed when the plate was at rest. Further the effect was examined through different parts of the plate, and no remarkable variation was found except in the neighborhood of the boundary of the plate, from which it may be concluded that the plate oscillates in a simple mode, having planes of loop and node as is required from the theory. A full account will be published in the *Scientific Papers of the Institute of Physical and Chemical Research.*

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The Institute of Physical and Chemical Research, Tokyo,
January 25, 1933.

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[2] C. S. Barrett, Phys. Rev. **38,** 832 (1931).

[3] S. Nishikawa, Y. Sakisaka and I. Sumoto, Phys. Rev. **38,** 1078 (1931).

Thermodynamic Calculations from Spectroscopic Data[1]

The most laborious step in the calculation of thermodynamic functions from spectroscopic data is the evaluation of the Q-sum, when the levels are not taken as those of a rigid rotator plus one or more harmonic oscillators. Giauque and Clayton[2] have shown how to calculate the rotational Q-sum for any one vibrational level, when the rotational levels are given by

$$\epsilon_r=B_v m^2+D_v m^4+F_v m^6+\cdots,$$

where $m=j+\frac{1}{2}$. The rotational constants can usually be represented by $B_v=B_0+\alpha v+\beta v^2$; $D_v=D_0+\gamma v$; $F_v=F_0+\delta v$. In any case, by the use of expressions similar to these, Eq. (5b) of Giauque and Clayton may be written as a power series expansion

$$Q_r(v)=K_0+K_1 v+K_2 v^2+\cdots,$$

where terms up to v^4 will ordinarily be sufficient. It is the purpose of this communication to show how the complete Q-sum may be obtained without term by term summation.

The energies of the vibrational states are

$$\epsilon_v=h(v\omega_e+v^2\omega_e x+\cdots).$$

The complete Q-sum is

$$Q=\sum_{v=0}^{\infty}Q_r(v)\exp\left[-(h/kT)(v\omega_e+v^2\omega_e x+\cdots)\right].$$

If we expand the anharmonic correction factor $\exp\left[-(h/kT)(v^2\omega_e x+\cdots)\right]$ as a power series in v^2, we get

$$Q=\sum_{v=0}^{\infty}P(v)z^v,$$

where $P(v)$ is a power series in v, and

$$z=e^{-h\omega_e/kT}.$$

This series can be summed, term by term, by using the following formulas.

$$(1-z)\sum_{v=0}^{\infty}z^v=1,$$

$$(1-z)^2\sum_{v=0}^{\infty}vz^v=z,$$

$$(1-z)^3\sum_{v=0}^{\infty}v^2z^v=z(1+z),$$

$$(1-z)^4\sum_{v=0}^{\infty}v^3z^v=z(1+4z+z^2),$$

$$(1-z)^5\sum_{v=0}^{\infty}v^4z^v=z(1+11z+11z^2+z^3),$$

$$(1-z)^6\sum_{v=0}^{\infty}v^5z^v=z(1+26z+66z^2+26z^3+z^4).$$

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[2] Giauque and Clayton, J. Am. Chem. Soc. **54,** 1731 (1932).

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,

$$Q = \sum_{u=0}^{\infty}\sum_{v=0}^{\infty} s^u t^v (1 + au^2 + buv + cv^2)$$

$$= ST + as(1+s)S^3T + bstS^2T^2 + ct(1+t)ST^3,$$

where

$$s = e^{-h\omega_1/kT} \qquad S = 1/(1-s),$$

$$t = e^{-h\omega_2/kT} \qquad T = 1/(1-t),$$

$$a = hx\omega_1/kT \qquad b = hy/kT \qquad c = hz\omega_2/kT.$$

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

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

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

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_r 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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Light Excitation in Neon by Lithium Ions

In view of the recent experiments of Beeck[1] 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 Keller[4] 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 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

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

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