

The Energy Levels and Thermodynamic Functions of the Fourth Power Oscillator

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evident from the study of electron emission as a function of the temperature of the fluorine coated filament that an extremely stable layer is formed which does not desorb below 2600°K. This corresponds to Roberts' first layer. It would be expected that any holes in this film would be filled by fluorine molecules, corresponding to Roberts' second layer. At elevated temperatures, these might either desorb as such, followed by dissociation, or they might dissociate in situ, leaving one atom adsorbed and desorbing the other atom of the molecule. This latter process would cause the surface to be completely covered by the stable atomic first layer.

The investigation of the fraction of the fluorine molecules dissociated seems to indicate that the fluorine is adsorbed onto a layer corresponding to Roberts' third layer. The precise nature of this layer, in the case of fluorine, is not yet clear.

A plausible explanation of the high rate of loss of tungsten is inherent in this picture. The fluorine atoms are sufficiently small as compared to the internuclear distance of tungsten so that an occasional atom or molecule from the second layer can slip between the atoms of the first

TABLE II. Rate of loss of tungsten from the filament.

Run	T, °K	P, μ	\dot{m}_w	\dot{m}_F/\dot{m}_w
2		6	7.0×10^{15}	566
3		2.4	8.4×10^{15}	190
7A	1990	1.0	7.3×10^{15}	90
7B	2120	1.2	1.1×10^{16}	72
7C	2250	2.4	1.25×10^{16}	128
7D	2350	3.0	1.03×10^{16}	194
7E	2075	2.4	1.13×10^{16}	140

layer, form chemical bonding with the tungsten, and sufficiently weaken the remaining tungsten-tungsten bonds so that the tungsten fluoride thus formed is readily evaporated.

CONCLUSION

Fluorine is found to form a very stable atomic layer on the surface of tungsten, which does not desorb below 2600°K. A less stable layer is believed to adsorb over the first layer. The fraction of the fluorine dissociated on the surface of the tungsten is exponential in temperature, and the rate of loss of tungsten from the surface is independent of temperature and of pressure, in the range 2000°K to 2400°K, and 1 to 6 microns of mercury pressure.

The Energy Levels and Thermodynamic Functions of the Fourth Power Oscillator

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The first six characteristic numbers of the reduced wave equation $\psi'' + (\lambda - \xi^4)\psi = 0$ have been calculated by a method of numerical integration. These values have been compared with the corresponding values obtained from the first, second, and third Wentzel-Kramers-Brillouin approximations. For the fourth, fifth, and sixth characteristic numbers, the third W.K.B. approximation is correct within 0.0001. The four thermodynamic functions $-(F-H_0)/RT$, $(H-H_0)/RT$, S/R , and C/R have been calculated over the range $h\nu_0/kT=0$ to 10. A previously reported maximum in the heat capacity function, C/R , does not exist.

THE potential $V(x)=ax^4$ is intermediate between the square law potential of the simple harmonic oscillator and the rectangular potential of the particle in a one-dimensional box with infinitely high walls. For this reason alone the energy levels of the fourth power oscillator are of interest. In addition, some molecules may

contain a vibration with a fourth power potential. For example, the twisting motion of the bridge structure in the aluminum halide dimers and in diborane may be of this type. Bell¹ has discussed the energy levels and the heat capacity of the fourth power oscillator. There are, how-

¹ R. P. Bell, Proc. Roy. Soc. A183, 328 (1944).

TABLE I.

Trial λ	$I(\lambda)$	N	$d\lambda/dN$	Corrected λ (λ_n)
1	3.046 9			1.060 5
2	3.109 0			
3	3.171 9			
4	3.236 2			3.799 8
1.000 000	3.047 164			
1.060 5	3.050 871 3	1.000 067 6	2.03	1.060 363
1.060 363	3.050 864 6	1.000 000 8	2.01	1.060 361
3.799 8	3.223 352 8	2.000 038 4	3.30	3.799 673
7.414 4	3.449 31	2.989 65	3.943	7.455 2
11.612	3.680 88	3.992 60	4.417	11.644 7
16.234	3.893 93	3.994 03	4.806	16.262 7
7.455 2	3.451 616	2.999 869	3.943	7.455 72
11.644 9	3.682 524	4.000 033	4.417	11.644 75
16.234	3.894 075	4.994 215	4.806	16.261 8
21.214	4.089 277	5.995 249	5.140	21.238 4

ever, a number of errors in his work which invalidate some of his results.

NUMERICAL INTEGRATION

The wave equation for the fourth power oscillator

$$(d^2\psi/dx^2) + (8\pi^2 m/h^2)(E - ax^4)\psi = 0 \quad (1)$$

is readily transformed into the reduced equation

$$(d^2\psi/d\xi^2) + (\lambda - \xi^4)\psi = 0 \quad (2)$$

by the substitutions

$$\xi = (8\pi^2 ma/h^2)^{1/6} x, \quad (3)$$

$$\lambda = (1/a)(8\pi^2 ma/h^2)^{2/3} E. \quad (4)$$

The numerical method given by Milne² is very convenient for the solution of this equation. The auxiliary differential equation

$$(d^2w/d\xi^2) + (\lambda - \xi^4)w - \lambda w^{-3} = 0, \quad (5)$$

which differs from Eq. (2) by the addition of the last term $(-\lambda w^{-3})$, is set up. The initial conditions $w(0) = 1$ and $w'(0) = 0$ are imposed in order to simplify the solution of Eq. (5). The following relationship exists between ψ and w for all values of λ :

$$\psi(\xi) = Cw(\xi) \sin \left\{ \lambda^{1/2} \int_{-\infty}^{\xi} w^{-2} d\xi \right\}. \quad (6)$$

Equation (5) is not a characteristic value equation; for all values of λ , w increases slowly from

² W. E. Milne, Phys. Rev. **35**, 863 (1930).

its initial value of unity while $|\xi| < \lambda^{1/2}$, then increases very rapidly for $|\xi| > \lambda^{1/2}$. As ξ approaches $-\infty$, ψ approaches zero; however, as ξ approaches $+\infty$, ψ approaches zero only if

$$\lambda^{1/2} \int_{-\infty}^{\infty} w^{-2} d\xi = N\pi, \quad (7)$$

where N is an integer. Fortunately, the integral

$$I(\lambda) = \int_{-\infty}^{\infty} w^{-2} d\xi \quad (8)$$

is not very sensitive to the value of λ . Equation (5) can be integrated numerically for a number of trial values of λ ; the values of λ that will make N of Eq. (7) an integer can then be determined by interpolation. These values of λ are the characteristic numbers (eigenvalues) of Eq. (2), and the corresponding functions $\psi(\xi)$ from Eq. (6) are characteristic functions (eigenfunctions).

It is advantageous to use the best approximations available for trial values of λ . Initially we used the four decimal values $\lambda_0 = 1.0605$ and $\lambda_1 = 3.7998$ which were calculated by Milne² by this same method. For the higher quantum states, we used the values given by the first Wentzel-Kramers-Brillouin approximation:^{1,3}

$$\lambda_{In} = 2.185069(n + \frac{1}{2})^{4/3}, \quad (n = 0, 1, 2, 3, \dots). \quad (9)$$

For each trial value of λ , Eq. (5) was integrated numerically by a method also devised by Milne.^{4,5}

An interval of 0.1 in ξ was used. The necessary starting values of w were calculated from the expansion

$$w = 1 + \frac{1}{30}\xi^6 - \frac{\lambda}{420}\xi^8 + \frac{\lambda^2}{9450}\xi^{10} + \frac{315 - 4\lambda^3}{1,247,400}\xi^{12} + \dots, \quad (10)$$

which was obtained with the aid of the initial conditions $w(0) = 1$ and $w'(0) = 0$, Eq. (5), and Maclaurin's series.

³ J. L. Dunham, Phys. Rev. **41**, 713 (1932).

⁴ W. E. Milne, Am. Math. Mo. **40**, 322 (1933).

⁵ Marchant Methods MM 216A, Marchant Calculating Machine Company, Oakland, California (1943).

The integration of Eq. (5) was carried out by means of five point open and closed Milne-Steffensen⁴ double integration formulas. At the end of every five complete cycles ($\Delta\xi=0.5$) an over-all check on the accumulated error in w was made by means of the eleven point closed formula:⁶

$$w_{i+10} = 2w_{i+5} - w_i + h^2 \sum_{n=0}^{10} C_n w''_{i+n}, \quad (11)$$

$$\begin{aligned} C_0 = C_{10} &= 2,144,850/38,320,128 \\ &= 0.055\,971\,890, \\ C_1 = C_9 &= 44,122,500/38,320,128 \\ &= 1.151\,418\,388, \\ C_2 = C_8 &= 59,426,250/38,320,128 \\ &= 1.550\,784\,225, \\ C_3 = C_7 &= 150,630,000/38,320,128 \\ &= 3.930\,832\,381, \\ C_4 = C_6 &= 98,902,500/38,320,128 \\ &= 2.580\,954\,323, \\ C_5 &= 247,551,000/38,320,128 \\ &= 6.460\,077\,586. \end{aligned}$$

The symbol h is the tabular interval; in this case, $\Delta\xi=0.1$.

Sufficient figures were carried in each integration to give $w^{-2}(\xi)$ to the desired accuracy, which was six, four, and five decimal places, respectively, in the three series of integrations that were performed. Since $w(\xi)$ is a symmetric function and increases rapidly with ξ after $\xi > \lambda^{\frac{1}{2}}$, it was necessary to integrate Eq. (5) only from $\xi=0$ to about 3.0. The integrals $I(\lambda)$ were evaluated by both Simpson's rule and Weddle's rule.

In Table I are given the various trial values of λ , the corresponding values of $I(\lambda)$, N , $d\lambda/dN$, and the derived characteristic numbers (λ_n). The first four rows are from Milne.² These values were used to calculate $d\lambda/dN$ for use with our integrations with Milne's values of λ_0 and λ_1 .

As can be seen from Table I, some of the corrected λ 's were used as trial λ 's in reintegrations of Eq. (5) in order to effect a check and improvement in their values. In the integration with trial=11.6449, the seven point closed double

integration formula

$$w_{i+6} = w_{i+5} + w_{i+1} - w_i + h^2 \sum_{n=0}^6 C_n w''_{i+n}, \quad (12)$$

$$\begin{aligned} C_0 = C_6 &= 787/12096 = 0.065\,062\,831, \\ C_1 = C_5 &= 12162/12096 = 1.005\,456\,349, \\ C_2 = C_4 &= 9789/12096 = 0.809\,275\,794, \\ C_3 &= 15004/12096 = 1.240\,410\,052, \end{aligned}$$

which was calculated by one of us,⁷ was used in place of the five point closed formula.⁴ This provided an answer to the question of whether the five point closed integration formula was sufficient to give $w(\xi)$ to the desired accuracy. Apparently the answer is in the affirmative, for the value of λ_3 was changed only slightly. The last digit of the corrected λ 's given in Table I is probably not significant.

It was discovered later in this work that the third W.K.B. approximation (see below) apparently provides very good values for the higher characteristic numbers. An elaborate integration was begun, with a trial $\lambda_{10} = 50.256\,255$, in which eight decimal places were carried and a nine point closed integration formula used. About two-thirds of the way through this integration it was discovered that the five, seven, nine, and eleven point integration formulae gave results in each cycle differing in the sixth or seventh decimal place of w . This behavior is decidedly not characteristic of a smooth function, but indicates the presence of rapidly oscillating higher derivatives. Numerical differences showed that this is just the situation in the fourth and sixth derivatives. Curiously enough, the number of such oscillations in the higher derivatives of w is about the same as would be expected in the corresponding derivatives of ψ . This was found to be true for the lower quantum states also. Although w appears to be smooth and continuously concave upward, the oscillatory nature of ψ is hidden in the higher derivatives of w .

This effect does not invalidate the integrations for the values of λ which are given. It does set an upper limit on the accuracy that may be attained (for a given integration interval h) and prevents Milne's method from being used on the higher quantum states.

⁶ This equation was calculated from the coefficients given by H. E. Salzer, J. Math. Phys. **24**, 135 (1945).

⁷ Marchant Methods MM 216B, Marchant Calculating Machine Company, Oakland, California (1946).

THE WENTZEL-KRAMERS-BRILLOUIN SOLUTION

Although much work has been done in recent years on the W.K.B. solution to the wave equation,^{8, 9, 12} it seems that no comparisons have been made between the exact energy levels of a particular wave equation and the levels given by the higher approximations of the W.K.B. method.

For the potential $v(x) = a|x|^q$, is quite practicable to carry the W.K.B. solution out to the third approximation. In the case of the harmonic oscillator, of course, the exact values of the energy levels are given by the first approximation of the W.K.B. method. It was thought that a comparison of the numerically integrated values of the characteristic numbers for the fourth-power oscillator with those given by the W.K.B. method would be considerable interest.

Dunham³ has given the expression for the first three W.K.B. approximations to the energy levels of the wave equation

$$-\frac{\hbar^2}{8\pi^2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad (13)$$

in the form

$$\begin{aligned} (n + \frac{1}{2})2\pi \left(\frac{\hbar^2}{8\pi^2m} \right)^{\frac{1}{2}} &= \oint (E - V)^{\frac{1}{2}} dx \\ &- \frac{1}{32} \frac{\hbar^2}{8\pi^2m} \oint V'^2 (E - V)^{-5/2} dx \\ &- \frac{1}{2048} \left(\frac{\hbar^2}{8\pi^2m} \right)^2 \oint [49V'^4 (E - V)^{-11/2} \\ &- 16V'V''' (E - V)^{-7/2}] dx. \quad (14) \end{aligned}$$

In the terms of the local momentum variable

$$p = [2m(E - V)]^{\frac{1}{2}}, \quad (15)$$

this equation assumes a somewhat simplified

form:

$$\begin{aligned} n + \frac{1}{2} &= -\frac{1}{\hbar} \oint p dx + \frac{1}{\hbar} \left(\frac{\hbar}{2\pi i} \right)^2 \oint (p')^2 p^{-3} dx \\ &+ \frac{1}{\hbar} \left(\frac{\hbar}{2\pi i} \right)^4 \left[-\frac{1}{32} \oint (p'')^2 p^{-5} dx \right. \\ &\quad \left. + \frac{15}{128} \oint (p')^4 p^{-7} dx \right]. \quad (16) \end{aligned}$$

Titchmarsh (see reference 12, pp. 136, 137) has pointed out that this is only apparently an expansion in powers of $\hbar/2\pi i$. For example, with the potential $V(x) = a|x|^q$, the substitutions:

$$\xi = \left(\frac{8\pi^2ma}{\hbar^2} \right)^{1/(q+2)} x, \quad (17)$$

$$\lambda = -\frac{1}{a} \left(\frac{8\pi^2ma}{\hbar^2} \right)^{q/(q+2)} E, \quad (18)$$

reduce Eqs. (13) and (16) to

$$\frac{d^2\psi}{d\xi^2} + (\lambda - |\xi|^q)\psi = 0 \quad (19)$$

and

$$\begin{aligned} n + \frac{1}{2} &= \frac{1}{2\pi} \left\{ \oint (\lambda - |\xi|^q)^{\frac{1}{2}} d\xi \right. \\ &- \frac{q^2}{32} \oint (\lambda - |\xi|^q)^{-5/2} |\xi|^{2q-2} d\xi \\ &+ \left[\frac{11q^4}{2048} \oint (\lambda - |\xi|^q)^{-11/2} |\xi|^{4q-4} d\xi \right. \\ &- \frac{q^3(q-1)}{128} \oint (\lambda - |\xi|^q)^{-9/2} |\xi|^{3q-4} d\xi \\ &\left. \left. - \frac{q^2(q-1)^2}{128} \oint (\lambda - |\xi|^q)^{-7/2} |\xi|^{2q-4} d\xi \right] \right\}. \quad (20) \end{aligned}$$

The parameter $\hbar/2\pi i$ has disappeared in the reduced W.K.B. expansion of Eq. (20). Dunham³ has indicated that the W.K.B. approximations to the energy levels of an oscillator become better as the mass of the oscillator increases. This cannot be true in general, however, since mass does not appear in Eq. (20). The characteristic numbers or reduced energy levels from Eq. (20)

⁸ G. D. Birkhoff, Bull. Am. Math. Soc. **39**, 681 (1933).

⁹ R. E. Langer, Bull. Am. Math. Soc. **40**, 545 (1934).

¹⁰ E. C. Kemble, Phys. Rev. **48**, 549 (1935).

¹¹ R. E. Langer, Phys. Rev. **51**, 669 (1937).

¹² E. C. Titchmarsh, *Eigenfunction Expansions* (Clarendon Press, Oxford, 1946).

are the same for all oscillators with a given q . Any particular level must be in error by some percentage which is independent of the mass of the system.

The contour integrals of Eq. (20) are readily evaluated in terms of the gamma-function

$$n + \frac{1}{2} = \frac{1}{2\pi} \left\{ \frac{4}{q} \frac{\Gamma\left(\frac{3}{2}\right)\Gamma\left(\frac{1}{q}\right)}{\Gamma\left(\frac{3}{2} + \frac{1}{q}\right)} \lambda^{\frac{1}{2} + (1/q)} - \frac{q}{8} \frac{\Gamma\left(-\frac{3}{2}\right)\Gamma\left(2 - \frac{1}{q}\right)}{\Gamma\left(\frac{1}{2} - \frac{1}{q}\right)} \lambda^{-\frac{1}{2} + (1/q)} - \frac{q^2(q-1)(2q+3)}{1536} \frac{\Gamma\left(-\frac{5}{2}\right)\Gamma\left(2 - \frac{3}{q}\right)}{\Gamma\left(-\frac{1}{2} - \frac{3}{q}\right)} \lambda^{-\frac{3}{2} + (1/q)} \right\} \quad (21)$$

For the case which we have investigated, $q=4$, ($V(x)=ax^4$), Eq. (21) reduces to

$$n + \frac{1}{2} = 0.55641 \, 78941 \lambda^{3/4} - 0.04767 \, 24852 \, 5 \lambda^{-3/4} + 0.01195 \, 42906 \, 9 \lambda^{-9/4}. \quad (22)$$

If only the first term on the right-hand side of Eq. (22) is retained, we have the so-called W.K.B. first approximation. The inclusion, in addition, of the second term gives the second W.K.B. approximation. The complete equation gives the third approximation. We have designated λ as a function of n from these three approximations as λ_{In} , $\lambda_{II n}$, and $\lambda_{III n}$, respectively.

It can be seen from Table II that the values of λ_{In} agree fairly well with those of the true characteristic numbers. For the fourth power oscillator, λ_{In} seems to be a lower limit to λ_n , although this point has not been proved. Titch-

TABLE II.

n	λ_{In}	$\lambda_{II n}$	$\lambda_{III n}$	λ_n (numerical integration)
0	0.867 145	0.980 766	0.951 643	1.060 361
1	3.751 920	3.810 330	3.808 377	3.799 673
2	7.415 988	7.455 795	7.455 282	7.455 72
3	11.611 525	11.644 990	11.644 779	11.644 75
4	16.233 615	16.261 937	16.261 829	16.261 83
5	21.213 653	21.238 438	21.238 375	21.238 4
6	26.506 336	26.528 515	26.528 474	
7	32.078 464	32.098 626	32.098 598	
8	37.904 472	37.923 021	37.923 001	
9	43.963 948	43.981 173	43.981 158	
10	50.240 152	50.256 266	50.256 255	
11	56.719 057	56.734 223	56.734 214	
12	63.388 708	63.403 054	63.403 047	
13	70.238 771	70.252 400	70.252 395	
14	77.260 210	77.273 205	77.273 201	
15	84.445 040	84.457 470	84.457 466	
16	91.786 147	91.798 070	91.798 067	

marsh¹² has given several equations which place upper and lower bounds on λ_n . These limits are actually too broad to be of any use in this case but do involve definite integrals closely related to the contour integrals of the first and second W.K.B. approximations. For example, Titchmarsh's equation (7.2.3), which places an upper bound on λ_n , is equivalent in the case of the fourth power oscillator to the first W.K.B. approximation, with the term $\frac{1}{2}$ replaced by unity. The second approximation, λ_{II} , is much better than the first approximation. The improvement, however, is not very marked in λ_{II0} and λ_{II1} . The third approximation gives perfect agreement with the characteristic numbers obtained by numerical integration, for $n=3, 4$, and 5, within their probable uncertainty. For $n=2$, either there is a small error in λ_2 (num. int.) or λ_{II2} is slightly better than λ_{III2} . Only a slight improvement is observed in λ_{III1} over λ_{II1} , and λ_{III0} is actually worse than λ_{II0} . It is interesting to note that the higher W.K.B. approximations improve in accuracy much more rapidly with increase in n than does the first approximation.

Bell¹ calculated, by means of a numerical difference method, the values of the first four characteristic numbers: $\lambda_0=1.09$, $\lambda_1=3.81$, $\lambda_2=7.36$, and $\lambda_3=11.40$. His errors are about the magnitude that he assigned (2 percent). In addition, he calculated the first five λ 's from both the first and second W.K.B. approximations. He also gives the single value, $\lambda_{III0}=1.15$, but

without the equations from which it was calculated. There are several errors, some of which may be typographical, in his W.K.B. work: (a) there is a missing factor of $1/2\pi$ in the second term of his Eq. (4); (b) the integral of his Eq. (6) is correct in form but is incorrectly evaluated numerically ($I_2=2.39628$, not 2.636); (c) there is a numerical error in his evaluation of λ_{II2} of

TABLE III.

x	$-(F-H_0)/RT$	$(H-H_0)/RT$	S/R	C/R
0	∞	0.7500	∞	0.7500
0.1	1.8486	0.7148	2.5634	0.7481
0.2	1.3631	0.6827	2.0457	0.7451
0.3	1.0921	0.6522	1.7443	0.7411
0.4	0.9085	0.6232	1.5317	0.7365
0.5	0.7724	0.5954	1.3678	0.7312
0.6	0.6662	0.5688	1.2350	0.7256
0.7	0.5805	0.5431	1.1236	0.7196
0.8	0.5096	0.5184	1.0279	0.7132
0.9	0.4499	0.4944	0.9443	0.7064
1.0	0.3990	0.4712	0.8702	0.6991
1.1	0.3551	0.4488	0.8040	0.6915
1.2	0.3170	0.4271	0.7442	0.6834
1.3	0.2837	0.4061	0.6898	0.6748
1.4	0.2543	0.3858	0.6401	0.6656
1.5	0.2284	0.3661	0.5945	0.6560
1.6	0.2054	0.3471	0.5525	0.6457
1.7	0.1849	0.3288	0.5137	0.6349
1.8	0.1666	0.3111	0.4777	0.6234
1.9	0.1502	0.2941	0.4443	0.6114
2.0	0.1356	0.2777	0.4133	0.5988
2.2	0.1106	0.2469	0.3574	0.5719
2.4	0.0903	0.2186	0.3089	0.5430
2.6	0.0738	0.1928	0.2666	0.5124
2.8	0.0604	0.1694	0.2298	0.4806
3.0	0.0495	0.1483	0.1978	0.4481
3.2	0.0405	0.1294	0.1699	0.4152
3.4	0.0332	0.1125	0.1457	0.3826
3.6	0.0272	0.0976	0.1248	0.3507
3.8	0.0223	0.0844	0.1066	0.3197
4.0	0.0182	0.0727	0.0910	0.2900
4.2	0.0149	0.0626	0.0775	0.2619
4.4	0.0122	0.0537	0.0660	0.2355
4.6	0.0100	0.0460	0.0560	0.2109
4.8	0.00821	0.0392	0.0475	0.1882
5.0	0.00672	0.03356	0.04028	0.16735
5.5	0.00408	0.02242	0.02650	0.12305
6.0	0.00248	0.01485	0.01733	0.08896
6.5	0.00150	0.00976	0.01126	0.06339
7.0	0.00091	0.00638	0.00729	0.04462
7.5	0.00055	0.00415	0.00470	0.03109
8.0	0.00033	0.00268	0.00301	0.02146
8.5	0.00020	0.00173	0.00193	0.01470
9.0	0.00012	0.00111	0.00123	0.00999
9.5	0.00007	0.00071	0.00078	0.00675
10.0	0.00004	0.00045	0.00049	0.00454

about 0.06. The net effect of all of these errors led Bell to the erroneous conclusion that the second W.K.B. approximation is no improvement on the first. His bad value for λ_{III0} probably discouraged him from a further investigation of the third approximation.

THERMODYNAMIC FUNCTIONS

The molal thermodynamic functions

$-(F-H_0)/RT$, $(H-H_0)/RT$, S/R , and C/R

were calculated as functions of the variable $x = h\nu_0/kT$. In this equation ν_0 represents the frequency that would be observed in a transition between the two lowest energy levels of a fourth power oscillator. The energy levels (E_n) of any particular fourth power oscillator are proportional to the corresponding characteristic numbers (λ_n) of the reduced equation. Therefore, we have

$$\frac{E_n - E_0}{kT} = \frac{\lambda_n - \lambda_0}{\lambda_1 - \lambda_0} \frac{E_1 - E_0}{kT} = \frac{\lambda_n - \lambda_0}{\lambda_1 - \lambda_0} x. \quad (23)$$

The partition function is given by the summation

$$Q = \sum_{n=0}^{\infty} \exp\left(-\frac{\lambda_n - \lambda_0}{\lambda_1 - \lambda_0} x\right). \quad (24)$$

From $x=0.5$ to $x=10.0$ the partition function and its derivatives were summed directly, with enough figures carried to give the thermodynamic functions to six significant figures. The thermodynamic functions were then rounded to four decimal places in the final tables up to $x=5.0$, and to five decimal places from $x=5.0$ to 10.0.

The values of λ_n that were used in these summations are as follows: (a) for λ_0 , λ_1 , λ_2 , λ_3 , λ_4 , and λ_5 , the values determined by numerical integration and given in the last column of Table II, (b) for λ_6 and higher λ_n 's, the approximations λ_{IIIn} , rounded to four decimal places. These values of λ_{IIIn} agree with those of λ_{IIIn} within that extent, and probably represent λ_n to better than 0.0001.

For $x=0.5$, it was necessary to sum the partition function and its derivatives to the term in λ_{16} . For $x<0.5$, direct summation became too laborious. The summations in this range were made by means of the Euler-Maclaurin summa-

tion formula. First the summation

$$Q_I = \sum_{n=0}^{\infty} \exp\left(-\frac{\lambda_{In} - \lambda_0}{\lambda_1 - \lambda_0}\right) \\ = \exp\left(\frac{\lambda_0 - \lambda_{I0}}{\lambda_1 - \lambda_0}\right) \\ \times \sum_{n=0}^{\infty} \exp\left(-\frac{\lambda_{In} - \lambda_{I0}}{\lambda_{I1} - \lambda_{I0}} \left[\frac{\lambda_{I1} - \lambda_{I0}}{\lambda_1 - \lambda_0} x\right]\right) \quad (25)$$

was evaluated, through the Euler-Maclaurin term in the fifth derivative of the exponential. This partition function is based on the same zero of energy as the correct partition function [Eq. (24)] and has the same independent variable, x (*not* $(E_{I1} - E_{I0})/kT$). It differs from the correct partition function in that it contains the W.K.B. first approximation characteristic numbers instead of the true λ_n 's. Since the final expression for Q_I is rather complicated and is probably not of general interest, it will not be given here.

For large values of n , λ_{In} approaches λ_n asymptotically; even for moderate values of n , λ_{In} , and λ_n do not differ very much. The partition function Q_I leads, therefore, to nearly correct values of the thermodynamic functions when x is small. This residual error was removed by subtracting from Q_I a sufficient number of exponentials in λ_{In} and replacing them with corresponding exponentials in λ_n :

$$Q = Q_I - \sum_{n=0}^{\sim 6} \exp\left(-\frac{\lambda_{In} - \lambda_0}{\lambda_1 - \lambda_0} x\right) \\ + \sum_{n=0}^{\sim 6} \exp\left(-\frac{\lambda_n - \lambda_0}{\lambda_1 - \lambda_0} x\right). \quad (26)$$

The values of the thermodynamic functions obtained in this manner agreed with those obtained by direct summation within 0.0001 at $x=0.5$. The values for smaller values of x should there-

fore be correct. Table III gives a summary of the four thermodynamic functions as functions of x .

It can be seen from the data given in Table III that the fourth power oscillator thermodynamic functions vary (qualitatively) with x in about the same way as do the corresponding functions of the harmonic oscillator. The most striking difference is that, as was pointed out by Bell,¹ the high temperature limiting value of the heat capacity function (C/R) and the heat content function $[(H-H_0)/RT]$ is 0.75 instead of unity.

Bell gave a short table of C/R . There is a considerable systematic error in his calculation, however. He found a maximum in C/R in the neighborhood of $x=1.0$. This maximum does not exist. Not enough details are given for us to determine the source of his error; it does not lie in the somewhat rough λ_n 's that he used. A partition function summed over Bell's set of λ_n 's yields a heat capacity function in good agreement with our work.

TRANSITION PROBABILITIES

After the characteristic numbers $\lambda_0=1.060361$, $\lambda_1=3.799673$, and $\lambda_3=11.64475$ were determined, the corresponding functions $w(\xi, \lambda)$ were inserted in Eq. (6). The indicated integration was performed up to each tabular value of ξ . In this way we obtained the unnormalized characteristic functions ψ_0 , ψ_1 , and ψ_3 at intervals of 0.1 in ξ . These functions were normalized and the transition integrals evaluated:

$$\int_{-\infty}^{\infty} \psi_0 \psi_1 \xi d\xi = 0.6008, \quad (27)$$

$$\int_{-\infty}^{\infty} \psi_0 \psi_3 \xi d\xi = 0.0325. \quad (28)$$

The third harmonic transition integral is only 5.4 percent of the fundamental integral. These values differ considerably from those given by Bell: 1.41 and 0.015, respectively.