the film was stationary, measured back from the new auxiliary spark line made with film in motion, located the point on the film at which the light point was when the spark passed in the bomb.

Summary

A diaphragm indicator for measuring the pressures developed in explosions is described. Its essential advantages are sensitivity, freedom from hysteresis for the deflections employed, and constancy. A method of calibrating dynamically, without removing the diaphragm from the explosion chamber, is described in which pressures are released against the diaphragm in a time interval of the same order as in explosions. It is shown that for this type of diaphragm the observed deflections for a given range of pressures investigated are the same for dynamic as for static calibration.

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Thermal Equilibrium between Oxygen Molecules and Atoms[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

During the course of experiments carried out at the Pittsburgh Experiment Station of the U. S. Bureau of Mines on the direct determination of the specific heat of oxygen at high temperatures by exploding mixtures of ozone and oxygen,[4] it was necessary to know the degree of dissociation in order to obtain accurate values of the specific heats. Since this information is not available in the literature, we have set up an equation for the equilibrium constant of the reaction $2O \rightleftharpoons O_2$ expressed as

$$K_p = \frac{[p_{\text{at.}}]^2}{p_{\text{mol.}}} \tag{1}$$

One commences with the well-known fundamental thermodynamic equation

$$\Delta F = \Delta H - T\Delta S \tag{2}$$

For the condition of equilibrium between atoms and molecules of oxygen $\Delta F = 0$, and therefore

$$0 = (\Delta H/T) - \Delta S \tag{3}$$

The entropy per mole of each participant in the reaction is given by

$$S = C_{p_0} \ln T + \int_0^T \frac{C_{\text{vib}}}{T}\, dT - R \ln p + Ri + C_{p_0} \tag{4}$$

where C_{p_0} is the constant part of the specific heat at the temperature T,

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(4) Lewis and von Elbe, THIS JOURNAL, **55**, 511 (1933).

i. e., due to translation and rotation; $C_{\text{vib.}}$ is the specific heat due to vibrations of the molecule, p is the partial pressure of each constituent at equilibrium, i is the chemical constant of each constituent.

Equation 4 includes the Sackur equation for translational entropy and also the rotational entropy for the case that rotation is fully excited. This may be shown by comparison with the statistical formulas

$$S_{\text{trans.}} = {}^5/_2R \ln T - R \ln p + {}^3/_2R \ln m + R \ln [(2\pi)^{3/2}k^{5/2}/h^3] + R \ln g + {}^5/_2R \qquad (3a)$$

$$S_{\text{rot.}} = {}^2/_2R \ln T - R \ln (\text{symmetry number}) - R \ln \frac{h^2}{8\pi^3 Ik} + {}^2/_2R \qquad (3b)$$

Adding 3a and 3b results in equation 3, less the vibrational part, *viz.*

$$S_{\text{trans.}+\text{rot.}} = {}^7/_2R \ln T - R \ln p + Ri + {}^7/_2R \qquad (3c)$$

Giauque and Johnston[5] have calculated the entropy of molecular oxygen from 0°K. to 298°K. which includes $(S_{\text{trans.}+\text{rot.}+\text{vib.}} + i_{\text{mol.}})$ where $i_{\text{mol.}}$ is the chemical constant of the oxygen molecule. Their value for this at one atmosphere pressure is 49.03 entropy units which we shall employ. Equation 3 transforms to

$$0 = \frac{\Delta H}{T} - [2S_{\text{at.}} - (S_{\text{mol.}}|_{298}^{T} + 49.03)] \qquad (5)$$

where $S_{\text{at.}}$ represents the entropy of the oxygen atom and $S_{\text{mol.}}|_{298}^{T}$ is the part of the entropy of the oxygen molecule between 298°K. and T°K. This expands to

$$0 = \frac{\Delta H_0}{T} + \frac{\int_0^T 2C_{p_{\text{at.}}}}{T}\,\mathrm{d}T - \frac{\int_0^T C_{p_{\text{mol.}}}}{T}\,\mathrm{d}T - 2S_{\text{at.}} + S_{\text{mol}}|_{298}^{T} + 49.03 \qquad (6)$$

Substituting for the entropy, equation 4, one obtains

$$0 = \frac{\Delta H_0}{T} + \frac{\int_0^T 2C_{p_{\text{at.}}}}{T}\,\mathrm{d}T - \frac{\int_0^T C_{p_{\text{mol.}}}}{T}\,\mathrm{d}T - 2R\,[{}^5/_2 \ln T - \ln p_{\text{at.}} + i_{\text{at}} + {}^5/_2] + R\left[{}^7/_2 \ln T + \frac{1}{R}\int_0^T \frac{C_{\text{vib.}}}{T}\,\mathrm{d}T - \ln p_{\text{mol.}} + {}^7/_2 + i_{\text{mol.}} - \left({}^7/_2 \ln 298 + \frac{1}{R}\int_0^{298} \frac{C_{\text{vib.}}}{T}\,\mathrm{d}T - \ln 1 + {}^7/_2 + i_{\text{mol.}}\right)\right] + 49.03 \qquad (7)$$

The expression $\int_0^{298} (C_{\text{vib.}}/T)\,\mathrm{d}T$ is negligibly small. Transposing, dividing by R and changing to logs to the base 10

$$\log \frac{[p_{\text{at.}}]^2}{p_{\text{mol.}}} = -\frac{\Delta H_0}{2.3\,RT} + \frac{3.5}{2.3} + 5 \log T + \frac{2i_{\text{at.}}}{2.3} - 3.5 \log T + 3.5 \log 298 - \frac{49.03}{2.3\,R} - \frac{1}{2.3\,R}\int_0^T \frac{C_{\text{vib.}}}{T}\,\mathrm{d}T \qquad (8)$$

ΔH_0 is the heat of dissociation at absolute zero which is equal to 117,300 calories per mole.[6] This value is for dissociation from the $^3\Sigma$ state of the

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(5) Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

(6) Paschen, *Naturwissenschaften*, **34**, 752 (1930); Sommer, *ibid.*, **34**, 752 (1930); Frerichs, *Phys. Rev.*, **36**, 398 (1930).

oxygen molecule to the $^3P_2$ state of the atom (see below). The expression $\int_0^T (C_{\text{vib.}}/T)\,\mathrm{d}T$ can be evaluated by Einstein functions $(F - F_0)/T$.[7] There is practically no difference between the values so derived and the values derived from the spectroscopic vibrational–rotational levels of the molecule. This is known by a comparison of such calculations.[4] This also makes it unnecessary to account for the change of the moment of inertia I in $i_{\text{mol.}}$ for higher rotational levels (compare equation 3b). Using the value of 1556.4 cm.$^{-1}$ for the separation of the first vibrational level of the oxygen molecule[8] we obtain

$$\frac{\beta\nu}{T} = \frac{2229}{T}$$

from which $(F - F_0)/T$ can be evaluated. $i_{\text{at.}}/2.3$ is expressed by the well-known equation[9]

$$\frac{i_{\text{at.}}}{2.3} = -1.587 + 1.5 \log M + \log g \tag{9}$$

where M is the atomic weight of the oxygen atom and g is the statistical weight of the atomic state.

The value of g is derived in the following way. The ground level of the oxygen atom is a triplet state in which the three terms $^3P_2$, $^3P_1$ and $^3P_0$ are separated by small energy differences: $^3P_2 - {}^3P_1 = 447$ calories, $^3P_2 - {}^3P_0 = 635$ calories. The multiplicity of the separate terms can be obtained from measurements of magnetic susceptibility made by Kurt and Phipps.[10] They find a multiplicity of 5 for the $^3P_2$ term, 3 for $^3P_1$ and 1 for $^3P_0$.

The statistical weight g of the atomic state is given by the sum of the products of the multiplicity of the terms $^3P_2$, $^3P_1$ and $^3P_0$ and the probability of the atoms being in each of these states, referred to the lowest state $^3P_2$. Then

$$g = 5 + 3e^{-447/RT} + e^{-635/RT} \tag{10}$$

The complete equation for $\log K_p$ is

$$\log K_p = -\frac{117300}{4.571\ T} + 1.5 \log T - \frac{(^1/_8 F/T;\ \beta\nu/T = 2229/T)}{4.571} - 0.104 + 2 \log (5 + 3e^{-447/RT} + e^{-635/RT}) \tag{11}$$

However, equation 11 must be revised by the addition of another term relating to the oxygen molecule, for the following reasons.

In our experimental determination of the specific heat of oxygen up to 2500°K., the results show that the experimental values of the specific heats are always higher than those calculated from the vibrational–rotational levels of the normal state of the molecule[4] in the temperature range investi-

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(7) Landolt and Börnstein, Supplementary Vol. 1, p. 702.

(8) Mecke and Baumann, *Z. Physik*, **73**, 139 (1931); Babcock and Hoge, *Phys. Rev.*, **39**, 550 (1932).

(9) See, for example, A. Eucken, "Lehrbuch der chemischen Physik," Leipzig, 1930, pp. 246–247; or the constant part of equation 3a above.

(10) Kurt and Phipps, *Phys. Rev.*, **34**, 1357 (1929).

gated. The difference becomes more pronounced with increasing temperature. It has been pointed out[11] that this difference can be accounted for by the predicted metastable $^1\Delta$ level of the neutral oxygen molecule. It turns out that the separation of this level from the ground state $^3\Sigma$ is 0.75 ± 0.05 volt or 17,200 ± 1000 calories.

The ratio of the multiplicities of the $^1\Delta$ and $^3\Sigma$ states is $^1\Delta/^3\Sigma = {}^2/_3$.[11] We therefore obtain for the statistical weights an expression for the molecule similar to that found for the atom: namely

$$\log g_{\text{mol.}} = \log (3 + 2e^{-17,200/RT}) \tag{12}$$

This term, except that part representing the multiplicity of the $^3\Sigma$ state, namely, log 3, which is already included in Giauque and Johnston's value of the entropy of the oxygen molecule, must be subtracted from equation 11.

The revised equation for log K_p is then

$$\log K_p = -\frac{117,300}{4.571\ T} + 1.5 \log T - \frac{\left(\frac{1}{3}\frac{F}{T}; \frac{\beta\nu}{T} = \frac{2229}{T}\right)}{4.571} - 0.104 + 2 \log (5 + 3e^{-447/RT} + e^{-635/RT}) - \log \left(1 + \frac{2}{3}e^{-17,200/RT}\right) \tag{13}$$

We believe that this equation is valid up to 4000°K. and may apply up to 5000°K. without serious error. The following table contains the calculated values of log K_p, and the per cent. dissociation x for one atmosphere pressure up to 5000°K. The value of x is derived from the expression

$$K_p = \frac{4x^2}{1 - x^2} P \tag{14}$$

TABLE I

VALUES OF LOG K_p AND DEGREE OF DISSOCIATION OF OXYGEN AT ONE ATMOSPHERE PRESSURE

T, °K.	Log K_p	x, %	T, °K.	Log K_p	x, %
1400	−11.968	5×10^{-5}	2800	−2.495	2.83
1600	− 9.610	8×10^{-4}	3000	−1.858	5.88
1800	− 7.772	6.5×10^{-3}	3500	−0.577	24.9
2000	− 6.298	0.0353	4000	+0.379	61.3
2200	− 5.091	0.142	4500	+1.120	87.6
2400	− 4.078	0.452	5000	+2.715	96.4
2600	− 3.228	1.22			

Experimental proof for the correctness of the degree of dissociation is given by experiments on the specific heat of oxygen.[4] At high temperatures, say 2400°K., the experimental points are far above the values of specific heats calculated from the vibrational–rotational levels of the molecule. This is accounted for by dissociation and the $^1\Delta$ level contribution to the specific heat. While at lower temperatures the dissociation rapidly disappears, the $^1\Delta$ level contribution decreases slowly. Therefore, at lower temperatures the difference between experimental values and those

(11) Lewis and von Elbe, *Phys. Rev.*, 41, 678 (1932).

from the vibrational–rotational levels is due only to the $^1\Delta$ level contribution. One can determine the separation of the $^1\Delta$ level from the $^3\Sigma$ level, from the experimental points at lower temperatures, *i. e.*, about 2000°K., and plot the new specific heat values given by the $^1\Delta$ level curve up to 2400°K. From the difference between this curve and the weighted mean of a large number of experimental points at this temperature, one obtains the degree of dissociation given by the above formula.

Summary

A rigorous equation is derived for the equilibrium constant of the reaction $2O \rightleftharpoons O_2$ with the aid of optical data and new determinations of the specific heat of oxygen at high temperatures. A table is given for log K_p and the degree of dissociation up to 5000°K. Experimental proof for the correctness of the degree of dissociation is given.

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The Specific Heat of Oxygen at High Temperatures from Ozone Explosions and the Energy of the $^1\Delta$ Level of the Neutral Oxygen Molecule[1]

BY BERNARD LEWIS[2] AND GUENTHER VON ELBE[3]

The theory of specific heats of gases demands that at high temperatures they be represented by the classical translational and rotational values of the specific heats plus the vibrational contribution. As far as molecular vibrations can be considered to be harmonic they are represented simply by the Planck–Einstein equation for an harmonic oscillator. This equation expressing the mean vibrational specific heat of one mole of gas for one vibrational degree of freedom between 300°K. and T is given by

$$\bar{C}^{\,T}_{\mathrm{vib}_{300}} = \frac{1}{T-300}\left(\frac{\epsilon_0}{e^{\epsilon_0/RT}-1}\right) \tag{1}$$

where ϵ_0 is the energy in calories per mole of the first vibrational level of the degree of freedom of the molecule considered. Tables for this function are available for example in Landolt–Börnstein.[4]

For a more rigid calculation involving the anharmonic oscillations of the actual molecule, one would use the actual separations of the higher vibrational levels wherever these are available from spectroscopic data, using the same statistical principles underlying the Planck–Einstein formula.

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[4] Landolt-Börnstein, Supplementary Volume 1, p. 702.