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Influence of Electrode Material on Oxygen Overvoltage: A Theoretical Analysis

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Variations of overvoltage for oxygen evolution from one metal to another primarily result from variations in the energy of the bond M—OH. The overvoltage decreases approximately in a linear manner with increasing bond energy. This relationship is verified experimentally for Ag, Au, Cd, Co, Cu, Fe, Ni, Pb, Pd, and Pt, for electrolysis in one N potassium hydroxide at one amp cm^{-2}; the experimental data are those reported by Hickling and Hill. Bond energies for M—OH are calculated by three different thermodynamic cycles involving, respectively, the standard heat contents of the hydroxide, the oxide, and spectroscopic data for molecules MO. Variations of the energy of the bond M—OH, as the electrode is oxidized to a higher valence, also account for sudden breaks in plots of overvoltage against logarithm of current density. Finally, there is essentially no correlation between the oxygen overvoltage for different metals and the corresponding work functions.

IT is well known from experimental studies that the nature of electrode material has a profound influence on the kinetics of electrode processes. The interpretation of this effect is difficult except for relatively simple reactions such as the discharge of hydrogen or hydroxyl ions. The former reaction was studied in a previous paper,[1] and it was shown on a theoretical basis that the overvoltage for hydrogen ion discharge varies from one metal to another primarily because of variations in the heat of adsorption of atomic hydrogen. An interpretation of the effect of electrode material is given in this paper for the electrolytic production of oxygen in alkaline aqueous solution. Unfortunately, the experimental study and the quantitative interpretation of oxygen overvoltage are far less advanced than for hydrogen overvoltage,[2] but sufficient experimental data are available[3] to test an explanation of the effect of electrode material.

INITIAL AND FINAL STATES FOR HYDROXYL ION DISCHARGE

We shall assume that the discharge of hydroxyl ions can be represented by the reaction

$$M+H_2O-OH^--e\rightarrow M-OH+H_2O \qquad (1)$$

which is followed by a process yielding molecular oxygen. The nature of the latter process is immaterial if one assumes that reaction (1) is rate determining. This is undoubtedly the case when the overvoltage exceeds say 0.1–0.2 volt, i.e. when the effect of the backward electrode reaction can be neglected. As for hydrogen ion discharge,[1] the overvoltage for the evolution of oxygen can be written in the form (note changes in sign)

$$\eta=\frac{RT}{\alpha F}\ln\xi+\frac{\Delta H^{\ddagger}}{\alpha\lambda F}-\left(1-\frac{1}{\alpha\lambda}\right)\psi_0-e_0. \qquad (2)$$

Here α is the transfer coefficient for the discharge process, λ is the number of hydroxyl ions which are discharged when the rate determining reaction occurs once,[4] $\Delta H^{\ddagger}$ is the energy of activation for the discharge process, ψ_0 is the difference of potential across the diffuse part of the Stern double layer at unit activity of OH^- ions, e_0 is the difference of potential from electrode to the outer Helmholtz layer at the standard reversible potential for hydroxyl ion discharge, and ξ represents a group of terms, whose explicit form is not needed here, and which can be regarded as independent of electrode material. The quantity ξ includes the entropy of activation for the discharge process, which will be assumed to be independent of electrode material. The derivation of Eq. (2) is given by Kortüm and Bockris[5] for hydrogen overvoltage. The terms α, $\Delta H^{\ddagger}$, and λ in Eq. (2) could possibly depend on the electrode material, while e_0, which includes the work function of the electrode, definitely depends on the nature of the electrode.

The interpretation of the effect of electrode material thus requires the calculation of the energy of activation $\Delta H^{\ddagger}$. This energy could, in principle, be deduced from variations of energy along the reaction coordinate. Such a method was applied by various authors[1,6,7] in the case of hydrogen ion discharge. Unfortunately, spectroscopic and other data needed in such calculations are not available for the discharge of hydroxyl ion, but useful information about factors influencing the energy of activation can be obtained by considering simply the initial and final states.

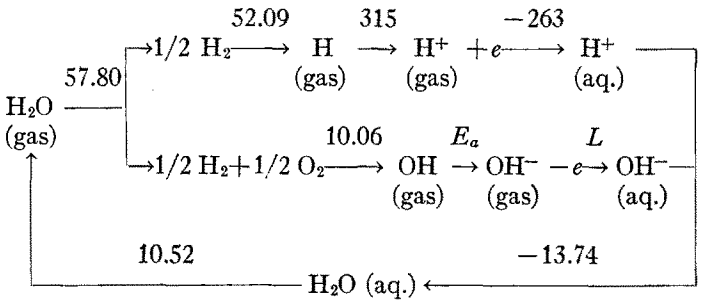
The initial state corresponds to one equivalent of hydroxyl ions in solution and the metal M from which one equivalent of electrons has been removed. The

* Postdoctoral fellow 1953–1954.
[1] P. Rüetschi and P. Delahay, J. Chem. Phys. **23**, 195 (1955).
[2] For a survey, see A. Hickling, Quart. Rev. **3**, 95 (1949).
[3] A. Hickling and S. Hill, Discussions Faraday Soc. **1**, 236 (1947).
[4] For hydrogen overvoltage when the discharge of hydrogen ion is the slow step $\lambda=1$.
[5] G. Kortüm and J. O'M. Bockris, *Textbook of Electrochemistry* (Elsevier Publishing Company, Inc., Houston, 1951), Vol. II, p. 430 Eq. 80. Note that e_0 was inadvertently dropped by the authors.
[6] See references in N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, London, 1941), third edition, 331ff.
[7] R. Parsons and J. O'M. Bockris, Trans. Faraday Soc. **47**, 914 (1951).

value of H_i is obtained from the following reactions

$$1/2\ H_2+1/2O_2\rightarrow OH\ (1\ atmos)$$
$$OH\ (1\ atmos)+e\rightarrow OH^-\ (gas)$$
$$OH^-\ (gas)\rightarrow OH^-\ (aq.)$$
$$OH^-\ (aq.)\rightarrow OH^-\ (double\ layer)$$
$$M(e)\rightarrow M+e.$$

The energy corresponding to the transfer of hydroxyl ions from solution to the double layer will be assumed to be negligible. This hypothesis is justified as was shown by Parsons and Bockris[7] for the discharge of hydrogen ions. The electron affinity and the heat of hydration of hydroxyl ion are not known, but the sum of these two quantities can be calculated from the following cycle



where E_a and L are the electron affinity and the heat of hydration of hydroxyl ion, respectively, and the numerical data are the changes in heat content.[8] The hydration energy of hydrogen ion, -263 kcal, is the average of two reported values, -250 kcal[9] and -276 kcal.[10]

One deduces from this cycle that $E_a+L=-168.7$ kcal, and the heat contents for the initial state is thus (in kcal)

$$H_i=\phi-158.7 \qquad (3)$$

where ϕ is the electronic work function of the electrode M.

As was pointed out in a similar calculation for hydrogen ion,[1] the surface potential[11] is neglected in the writing of Eq. (3).

The final state is defined as one equivalent of OH radicals bound to metal M. The corresponding heat contents H_f is derived from the cycle

$$1/2\ H_2+1/2\ O_2\ (1\ atmos)\rightarrow OH\ (1\ atmos)$$
$$OH\ (1\ atmos)+M\rightarrow M-OH$$
$$M-OH+H_2O\rightarrow H_2O-M-OH.$$

Thus

$$H_f=R-D(M-OH)+10.06 \qquad (4)$$

where H_f is in kcal, R is the energy of interaction between M—OH and water, D(M—OH) is the energy of the bond M—OH, and 10.06 kcal is the heat of formation of the hydroxyl radical. The interaction energy R is not known, and we shall assume that it is independent of the electrode material. This may be a rather coarse approximation.

[8] Taken from "Selected values of chemical thermodynamic properties," Series 1, National Bureau of Standards, 1949.
[9] Latimer, Pitzer, and Slansky, J. Chem. Phys. 7, 108 (1939).
[10] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).
[11] For references pertaining to surface potentials, see reference 2.

CALCULATION OF THE ENERGY OF THE M—OH BOND

The comparison of overvoltage values for different metals, i.e. the comparison of the corresponding $\Delta H^{\ddagger}$'s, requires values of the bond energy D(M—OH) appearing in Eq. (4). These energies are not known, but *approximate* values can be obtained by the following three methods.

First Method. From the following cycle

$$x/2\ H_2+x/2\ O_2+yM\rightarrow M_y(OH)_x$$
$$M_y\ (OH)_x\rightarrow M\ (cryst.)+x OH$$
$$x OH\rightarrow x/2\ H_2+x/2\ O_2$$

one deduces, by expressing that $\Sigma\Delta H^0=0$, the bond energy (in kcal)

$$D(M-OH)=10.06-\Delta H^0/x \qquad (5)$$

where 10.06 is the heat of formation of the hydroxyl radical, and ΔH^0 is the standard heat of formation of the hydroxide.

Second Method. The cycle is

$$xH_2+xO_2+yM\ (cryst.)\rightarrow M_yO_x+xH_2O\ (gas)$$
$$M_yO_x+xH_2O\ (gas)\rightarrow M_y\ (OH)_{2x}\ (cryst.)$$
$$M_y\ (OH)_{2x}\ (cryst.)\rightarrow yM\ (cryst.)+2xOH$$
$$yM\ (cryst.)+2xOH\ (gas)\rightarrow yM\ (cryst.)+xH_2+xO_2$$

and the resulting bond energy is (in kcal)

$$D(M-OH)=\frac{1}{2x}(-x\Delta H^0_{H_2O}-\Delta H^0_{M_yO_x}+2\times 10.06x) \qquad (6)$$

on the assumption that the heat of hydration of the oxide can be neglected. This is a reasonable simplifying assumption, and the bond energy is

$$D(M-OH)=38.96-\Delta H^0_{M_yO_x}/2x. \qquad (7)$$

TABLE I. Bond energies and pertaining data.

Metal	1st method H°[a]	x	D(M−OH)	2nd method H°[b]	x	D(M−OH)	3rd method D°[c]	x	D(M−OH)
Ag	...	...	...	...	...	...	41.5	1	60
Au	100.0	3	43.4	−9.65	3	35.8	...	...	...
Cd	133.3	2	76.8	60.8	2	69.4	88	2	53
Co	176.6	3	69.0	68.0	8/3	64.5	...	...	...
Cu	106.1	2	63.2	37.1	2	57.5	113	2	66
Fe	197.0	3	75.7	63.7	3	71.8	110	2	65
Ni	162.1	3	64.1	58.4	4	53.8	100	2	59
Pb	123.0	2	71.6	66.1	4	55.5	99	2	59
Pd	169.4	4	52.4	20.4	2	49.2	...	...	...
Pt	87.2	2	53.7	13.6	8/3	44.1	...	...	...

[a] Negative heat of formation of the hydroxide of valence x in kcal./mol. at 298.1°.
[b] Negative heat of formation of the oxide of valence x in kcal./mol. at 298.1°.
[c] Spectroscopic heats of dissociations of M−O in kcal./mol.

Third Method. The bond energy $D(M-OH)$ is calculated from spectroscopic data for the dissociation of the diatomic molecule M−O. The following cycle, in which all the species are in the gaseous form, is used

$$MO+H_2O \rightarrow M(OH)_2$$
$$M(OH)_2 \rightarrow M+2OH$$
$$M+2OH \rightarrow M+O+H+OH$$
$$M+O+H+OH \rightarrow MO+H_2O.$$

The corresponding bond energy $D(M-OH)$ is (in kcal)

$$D(M-OH)=\tfrac{1}{2}[D(M-O)+D(H-OH)-D(O-H)] \quad (8)$$

if one neglects the heat of hydration of the oxide (see second method). One has (in kcal)

$$D(H-OH)=52.09+10.06+57.80$$
$$D(O-H)=52.09+59.16-10.06$$

where 52.09 is one-half of the heat of dissociation of H_2, 10.06 the energy of formation of the hydroxyl radical, 57.80 the standard energy of formation of water, and 59.16 the standard energy of formation of hydroxyl ion. Thus

$$D(M-OH)=\tfrac{1}{2}[D(M-O)+18.76]. \quad (9)$$

The value of $D(M-OH)$ for silver cannot be calculated neither by the first method because the heat of formation of the hydroxide is not known, nor by the second method because silver atoms are associated in the oxides (Ag_2O, Ag_2O_2). The third method was modified, and the following cycle was used

$$M+2OH \rightarrow MOH+OH$$
$$MOH+OH \rightarrow MO+H_2O,$$

where all the species are in the gaseous form.

Bond energies calculated by the above three methods are listed in Table I. Thermodynamic data were taken from the Bureau of Standards Tables,[8] and spectroscopic data are from Herzberg[12] and Gaydon.[13] It is to be noted that the bond energy may vary markedly with the oxidation number. Thus $D(M-OH)$ calculated by the first method is 74.3 kcal for $Ni(OH)_2$ and 64.1 kcal for $Ni(OH)_3$. Likewise, one calculates by the second method values of $D(M-OH)$ of 66.2 kcal, 62.0 kcal, and 56.5 kcal from PbO, Pb_3O_4, and PbO_2, respectively. Generally, the higher is the oxidation number, the lower the bond energy.

OVERVOLTAGE *VERSUS* ENERGY OF THE BOND M−OH

If one assumes that $\alpha\lambda$ is the same for two metals 1 and 2, the difference in overvoltage for identical conditions of electrolysis is in view of Eq. (2)

$$\eta_1-\eta_2=\frac{1}{\alpha\lambda F}(\Delta H_1^{\ddagger}-\Delta H_2^{\ddagger})-[(e_0)_1-(e_0)_2]. \quad (10)$$

The quantity $[(e_0)_1-(e_0)_2]$ in Eq. (10) is equal to the difference of the work functions $(\phi)_2-(\phi)_1$. The term in $(\Delta H_1^{\ddagger}-\Delta H_2^{\ddagger})$ in Eq. (10) also contains the difference $(\phi)_1-(\phi)_2$ [see Eq. (3)], but the difference between the work functions should be multiplied by the product $\alpha\lambda$ in view of the definition of the transfer coefficient α. As a result, the difference between the ϕ_w's in Eq. (10) cancels, and *the difference in overvoltage for two metals is independent of the difference between the work functions of these metals.* This conclusion is valid provide that the mechanism of the electrode reaction is the same for metals 1 and 2 and that the transfer coefficient is also the same for the two metals. However, a small difference between the α's would be unimportant.

The difference between the energies of activation in Eq. (10) depends on the difference between the bond energies $D(M-OH)$ and the interaction energies between M−OH and water [see Eq. (4)]. As $D(M-OH)$ increases, the energy of activation decreases and the Morse curve for the energy $D(M-OH)$ becomes

[12] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1950), second edition.
[13] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1953).

steeper. Furthermore, the distance between the initial and final states along the reaction coordinate varies from one metal to another. Since the Morse curves cannot be calculated with the data now available, no detailed analysis similar to the one made for hydrogen ion[2] can be made.[14] However, the combination of these effects is such that the very *approximate* relationship

$$\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger} \approx D(\mathrm{M_2-OH}) - D(\mathrm{M_1-OH}) \qquad (11)$$

holds. This can be seen from the plot of overvoltage against $D(\mathrm{M-OH})$ in Fig. 1. Overvoltage values were taken from the paper of Hickling and Hill,[3] and bond energies are from Table I. Values of $D(\mathrm{M-OH})$ calculated by the above three methods are indicated for some metals to show the uncertainty on the energy data. The lowest values of bond energies, which often corresponds to the highest oxidation number of the metal, are generally preferred. This is because oxygen is

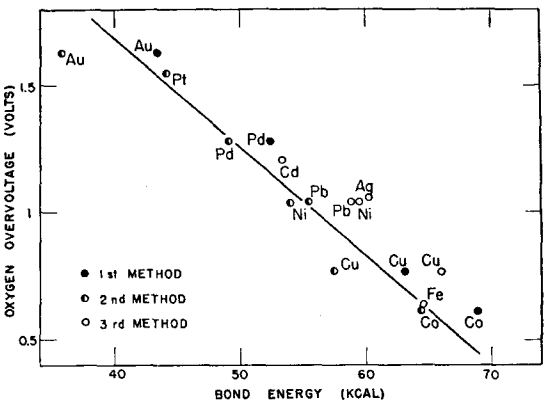


FIG. 1. Oxygen overvoltage against energy of the bond M—OH. Electrolysis at 25° in 1 *N* potassium hydroxide and at 1 amp cm^{-2}.

evolved at very positive potentials (about 1 to 1.5 volts *vs* N.H.E.) at the current density of 1 amp cm^{-2} corresponding to the data of Fig. 1. At such high *p*H's (1 *N* potassium hydroxide) and potentials, the metals of Fig. 1 are generally in their highest oxidation state.

Some values of the bond energies have not been plotted in Fig. 1 for the following reasons. The bond energy of 71.6 kcal for Pb obtained by the first method was not used because this datum corresponds to Pb(II) while lead is undoubtedly in the +4 state at the potentials corresponding to Fig. 1. The values of 53.7 kcal for Pt and 64.1 kcal for Ni were not plotted for the same reason. The values of $D(\mathrm{M-OH})$ obtained for iron by the first two methods were not used because they are higher than the value deduced from the third method. Finally, the value of 54.4 for cadmium was plotted

[14] The semiempirical method of J. O. Hirschfelder, [J. Chem. Phys. **9**, 645 (1941)] could be applied, but the resulting analysis does not go beyond the above approach. Hirschfelder's method was applied to hydrogen recombination at electrodes by K. E. Shuler and K. J. Laidler [J. Chem. Phys. **17**, 1212 (1949)] and to hydrogen ion discharge by R. Parsons [Z. Elektrochem. **55**, 111 (1951)].

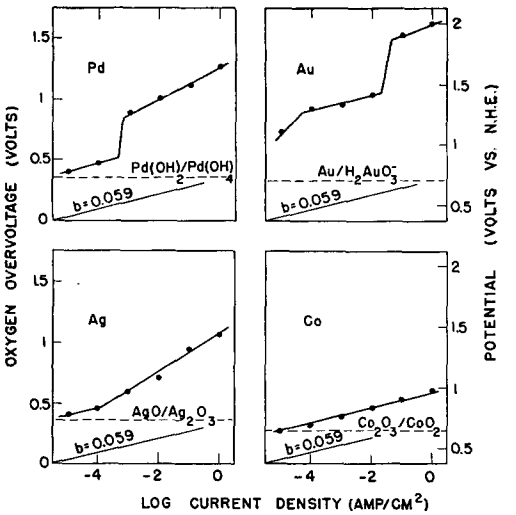


FIG. 2. Overvoltage against decimal logarithm of current density. Experimental data taken from Hickling and Hill (see reference 3).

because the values calculated by the first two methods are probably too high (by perhaps 20 kcal).

Despite the uncertainty in the values of bond energies, the foregoing considerations show that differences in the energy of the bond M—OH essentially account for variations of oxygen overvoltage from one metal to another under given conditions of electrolysis.

In view of Eqs. (10) and (11) the slope of the overvoltage *versus* bond energy line should be $-1/\alpha\lambda F$. Figure 1 yields the value $\alpha\lambda = 0.98$. This is of course only a very approximate value, but it agrees well with the experimental value of 1 which one deduces from experimental plots of overvoltage *versus* logarithm of current density. The latter plots yield straight lines provided that $\alpha\lambda$ does not vary with current density and that there is no change in the mechanism of the electrode process as the current is varied. The slope of this line is $b = 2.3RT/\alpha\lambda F$ or $b = 0.059/\alpha\lambda$ at 25° if decimal logarithms are used. The experimental slopes for Co, Fe, and Cu are virtually 0.059 at 1 amp cm^{-2}, and consequently $\alpha\lambda$ is very close to unity, which is precisely the value deduced from Fig. 1. The slopes *b* for Ag, Ni, and Pd at 1 amp cm^{-2} are 0.15, 0.15, and 0.13, respectively (Fig. 2). The corresponding overvoltages for a slope of $b = 0.059$ would be a few tenths of a volt lower, but this hardly changes the general trend of Fig. 1. These changes in slope probably result from the oxidation of the electrode to a higher valence as will be shown.

ENERGY OF THE BOND M—OH AND ANOMALIES IN OVERVOLTAGE *VERSUS* LOG*i* PLOTS

The dependence of the overvoltage on the energy of the bond M—OH also explains anomalies observed in plots of overvoltage against logarithm of current density. Figure 2, which was constructed from data of Hickling and Hill,[3] shows such anomalies for silver, palladium, and gold. The η *vs* log*i* plots are composed

of several linear segments with sudden variations of overvoltage. The slope of these segments may be the same (Au) or it may vary (Ag, Pd). For some metals such as cobalt the plot of η *vs* log$i$ yields a straight line over a wide range of current densities.

These sudden variations in overvoltage probably result from variations of the energy of the bond M—OH as the electrode is oxidized to a higher valence. This view is strongly supported by the fact that the sudden increases in overvoltage occur in the immediate vicinity of the equilibrium potentials for different oxidation states of the electrode. This is shown in Fig. 2 for palladium and gold.[15] In the case of silver a change in mechanism is primarily observed and λ varies from 2 to 1. No break is observed in the η *vs* log$i$ plot for cobalt because this metal is in its highest oxidation state at the potentials of Fig. 2.

[15] Equilibrium potentials taken from W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions* (Prentice-Hall, New York, 1952), second edition and G. Charlot, *Théorie et Méthode Nouvelle d'Analyse Qualitative* (Masson, Paris, 1949), third edition.

CONCLUSION

Variations of oxygen overvoltage from one metal to another under given conditions of electrolysis in aqueous alkaline solution primarily result from variations of the energy of the bond M—OH. Variations in this bond energy as the electrode is oxidized to a higher valence account for breaks observed in plots of overvoltage against the logarithm of current density.

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On the Structure of the Configuration Integral in the Statistical Mechanics of Pure Fluids*

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A form for the configuration integral is postulated. Its most important feature is the location of its zeros and poles in the complex volume plane. These lie on a contour which divides the real axis into distinct regions. The pressure, being expressed as an integral taken over this contour, can have different analytic forms on different parts of the real volume axis. It is shown that the asymptotic nature of a configuration integral of the assumed form is determined by the $p-v$ isotherms it produces, and the theory is worked out for isotherms derivable from a function of the van der Waals type with a classical critical point. The contour on which the zeros and poles of the configuration integral lie, and the density with which they are distributed, are determined explicitly in terms of these isotherms. The theory is illustrated in detail in the case of a simple equation of state.

THE thermodynamic functions for pure substances can be obtained from the logarithm of the partition function, in the limit of an infinite sample. The partition function has no zeros or singularities, in the case of a *finite* sample, at any physically meaningful values of its variables. Thus, the only way that the thermodynamic functions can show singularities characteristic of phase transitions, is for the partition function to have zeros, or singularities, or both, in the complex plane of one of its variables, and for some of these points to accumulate in the neighborhood of the real axis in the limit of an infinite number of particles. The details of such a process were worked out by Yang and Lee[1] for the grand partition function of the two-dimensional lattice gas in the complex fugacity plane.

In this paper, a number of assumptions will be made about the configuration integral in the complex volume plane. It will then be shown that the nature of all of the elements assumed to be present in the configuration integral of a macroscopic sample (the density with which its zeros and poles are distributed, the contour on which they lie, etc.) is completely determined by the pressure-volume isotherms to which such a configuration integral would give rise. The equation of state, then, determines the detailed asymptotic nature of the configuration integral provided the latter is of the assumed general structure. The assumptions which are made concerning its form appear to be the simplest possible, so in this way one obtains a knowledge of its probable structure which should aid materially its *a priori* evaluation.

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[1] C. N. Yang and T. D. Lee, Phys. Rev. 87, 404 (1952); T. D. Lee and C. N. Yang, Phys. Rev. 87, 410 (1952).

I. A POSTULATED FORM OF THE CONFIGURATION INTEGRAL AND A PRELIMINARY FORMULA FOR THE PRESSURE

Consider a classical system of N identical interacting particles in a volume Nv. Suppressing explicit reference to the temperature dependence, let $Q_N(v)$ and $p_N(v)$ be the configuration integral and the pressure in such a