THE ENERGETICS OF REACTIONS INVOLVING HYDROGEN PEROXIDE, ITS RADICALS, AND ITS IONS

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In discussions of free-radical reactions in solution it is necessary to know the energetic and the thermodynamic quantities involved in the primary steps. In aqueous solution these reactions frequently involve ions and ionised species of atoms and free radicals. In recent years great attention has been focused on the free radicals and ions arising from water and hydrogen peroxide. These species are H, OH, HO_2, O_2, H^+, OH^-, HO_2^-, and O_2^-. To understand the reactions of these entities in aqueous solution with each other and with metal ions we need fundamental quantities such as bond-dissociation energies, electron affinities, ionisation potentials, solvation energies, and the corresponding entropy changes.

In this Review we present values of the above quantities which we consider to be most firmly based and show how these quantities are derived from experimental data. We also give tables of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for most of the reactions of the above entities amongst themselves and with metal ions in different oxidation states which have been studied directly or discussed as steps in an overall reaction scheme.

I. The Bond-dissociation Energies in Hydrogen Peroxide.—(*a*) *The* HO....OH *Bond-dissociation Energy.* This has been obtained from the following cycle :

$$\begin{tikzcd}
H_2 \arrow[d, "-D_{H_2}"'] & + & O_2 \arrow[d, "-D_{O_2}"] \arrow[rr, "Q_f"] & & H_2O_2 \\
2H & + & 2O \arrow[rr, "2D_{OH}"'] & & 2OH \arrow[u, "D_{HO....HO}"']
\end{tikzcd}$$

whence

$$D_{HO....OH} = Q_f + D_{H_2} + D_{O_2} - 2D_{OH} \quad . \quad . \quad . \quad (1)$$

where the values of D_{H_2}, D_{O_2}, and D_{OH} used are those given in Table 1 ; $D_{HO....HO}$ is evaluated as 55·6 kcal. This value refers to the gas-phase reaction. Assuming that the heat of solution of OH is similar to the heat of condensation of water, we obtain for the solution phase a bond-dissociation energy of 46·7 kcal. (the heat of hydration of liquid H_2O_2 being taken as 0·7 kcal. ; Evans, Baxendale, and Uri [1]).

(*b*) *The* HOO....H *Dissociation Energy.* This may be evaluated from the following cycle :

$$\begin{tikzcd}
(H_2O_2)_g \arrow[r, "-D_{HO_2....H}"] & H \arrow[d, "(-I_H + S_{H^+})"'] & + & O_2H \arrow[d, "(E+S)_{HO_2}"] \\
(H_2O_2)_{aq.} \arrow[u, "-(\lambda + S)_{H_2O_2}"] \arrow[r, "Q"'] & H^+_{aq.} & + & HO^-_{2\,aq.}
\end{tikzcd}$$

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[1] *Trans. Faraday Soc.*, 1949, **45**, 236.

whence

$$D_{HO_2 \ldots H} = -Q - (\lambda + S)_{H_2O_2} + (-I_H + S_{H^+}) + (E_{HO_2} + S_{HO_2^-}) \quad . \quad (2)$$

The value of Q has been measured by Evans and Uri;[2] the value of $(\lambda + S)_{H_2O_2}$ is taken as 11·6 + 0·7 = 12·3 kcal.

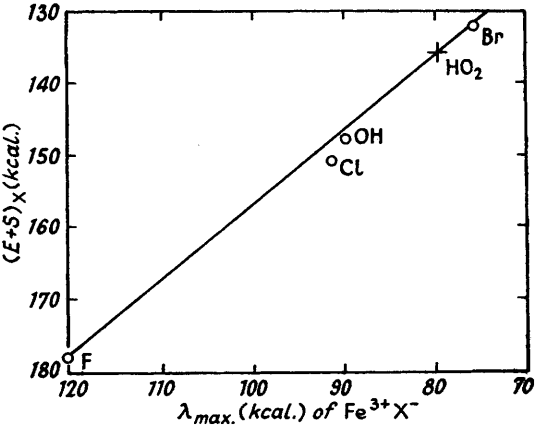
The unknown quantity remaining in this equation is $(E + S)_{HO_2}$. An idea of this value may be obtained from the energy of the absorption maximum in the spectrum of the $Fe^{3+}HO_2^-$ ion-pair complex in solution. The absorption spectra of ion-pairs of the type $Fe^{3+}X^-$ have been described as electron-transfer spectra, and the energy of the absorption maximum identified with the energy change of the reaction $Fe^{3+}X^- \xrightarrow{h\nu} Fe^{2+}X$. Under these conditions, because of the Franck–Condon principle, the position of the nuclei both in the ion-pair itself and in the solvation shell will be unchanged. The terms entering into the absorption energy can be seen from the following cycle:

$$\begin{tikzcd}
Fe^{2+}X \arrow[r, "-D^s_{Fe^{2+}X}"] & Fe^{2+} & +\ X \\
Fe^{3+}X^- \arrow[u, "-Nh\nu"] \arrow[r, "-D^s_{Fe^{3+}X^-}"] & Fe^{3+} \arrow[u, "J_{2-3}"] & +\ X^- \arrow[u, "-(E + S)_X"']
\end{tikzcd}$$

in which $D^s_{Fe^{3+}X^-}$ is the heat of formation of the normal ion-pair from the separate ions in solution. $D^s_{Fe^{2+}X}$ is the heat of formation of $Fe^{2+}X$ in a configuration in which the centres and the water molecules have exactly the same positions as in $Fe^{3+}X^-$. $D^s_{Fe^{2+}X}$ will therefore differ from the normal heat of formation of this entity by energy terms arising from the fact that neither the centres nor the water molecules are in their normal equilibrium configuration:

$$-Nh\nu = -D^s_{Fe^{3+}X^-} + D_{Fe^{2+}X} + J_{2-3} - (E + S)_X \quad . \quad . \quad (3)$$

From direct measurements of heats of formation of ion-pairs we know the value of $D^s_{Fe^{3+}X^-}$, and over the range of ions F^-, Cl^-, OH^-, HO_2^-, Br^- this value does not vary by more than ± 5 kcal. That the energy terms arising from the non-equilibrium configuration of $Fe^{2+}X$ are considerable is seen from a comparison of $Nh\nu$ and $[-D^s_{Fe^{3+}-X} + J - (E + S)_X]$ in cases where $J - (E + S)_X$ is known with some certainty. However, in spite of this, it is an experimental fact that the value of $(E + S)_X$ is approximately linear with $Nh\nu$ (see fig.). This experimental observation encourages



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[2] *Trans. Faraday Soc.*, 1949, **45**, 224.

us to interpolate a value of $(E + S)_{HO_2}$ from the known energies of the absorption maxima. This method leads to a value of $(E + S)_{HO_2} = 136$ kcal., which, used in equation (2), leads to a value of 102 kcal. for the bond-dissociation energy $HO_2....H$. This value seems to us to be—as we shall discuss later—in conformity with chemical evidence; although it has been derived through an argument involving values of $(E + S)$ for various ions, the value $D_{H....O_2H}$ is independent of the particular way in which the overall energy of the reaction $Fe^{2+} + \frac{1}{2}X_2 \rightarrow Fe^{3+} + X^-$ is split up between $J_{2\text{-}3}$ and $(E + S)_X$. From the cycle (2) it is seen that the value of $D_{HO_2....H} = 102$ kcal. applies to the gas phase, and in obtaining the corresponding value for bond dissociation in solution we have identified the heat of solution of HO_2 with that of hydrogen peroxide.

(*c*) *The* $D_{H....O_2}$ *Bond-dissociation Energy.* This is obtained from the following cycle:

$$\begin{tikzcd}
H_2O_{2g} \arrow[r, "-D_{H....O_2H}"] \arrow[d, "-Q_f"'] & H + HO_2 \\
H_2 + O_2 \arrow[r, "-D_{H_2}"] & H + \underbrace{H + O_2} \arrow[u, "D_{H....O_2}"']
\end{tikzcd}$$

whence

$$D_{H....O_2} = -D_{H....O_2H} + Q_f + D_{H_2} \quad . \quad . \quad . \quad (4)$$

Using the values of bond dissociation obtained above together with the data in Table 1(*a*), we have evaluated the bond-dissociation energy $D_{H....O_2}$ as 35·8 kcal. As we have indicated in the above discussion, when we obtain heats of dissociation or reaction in the gas phase from measurements in solution, heats of solution of free radicals are required. There are no direct measurements of such heats and we have had to make the assumption shown in Table 1(*b*).

TABLE 1 *

(*a*) *Dissociation processes*

Reaction	*D* (kcal.)	Reaction	*D* (kcal.)
$H_2 \rightarrow H + H$ . .	104·1	$HOH \rightarrow H + OH$ . .	120·7
$O_2 \rightarrow O + O$ . . .	118·2	$HO \rightarrow H + O$ . .	100·1

(*b*) *Heats of solution of radicals and molecules*

Radical or molecule	*Q* (kcal.)	Radical or molecule	*Q* (kcal.)
H_2O	10·5	H_2.	1·4
OH	10·5	H	1
HO_2	12·3	O_2	3·9
H_2O_2	12·3	O	2

* The data of Table I, with the exception of heats of solution of radicals, are based on the values listed by Bichowsky and Rossini [3] and recent spectroscopic work. We have assumed that $Q_s(HO_2) = Q_s(H_2O_2)$ and that $Q_s(OH) = Q_s(H_2O)$; the heats of solution of H and O will be very small and are estimated from trends in gas solubility as 1 and 2 kcal./mole, respectively.

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[3] "Thermochemistry" (Reinhold, 1936).

TABLE 2

Reaction	Heat (kcal.)	Reaction	Heat (kcal.)
(1) *Reactions in gas phase*			
$OH+H_2O_2 \rightarrow H_2O+HO_2$	19	$HO_2 \rightarrow H+O_2$	−36
$OH+HO_2 \rightarrow H_2O+O_2$	85	$H_2O_2 \rightarrow H+HO_2$	−102
$HO_2+H_2O_2 \rightarrow H_2O+OH+O_2$	30	$OH+OH \rightarrow H_2O_2$	56
$HO_2+HO_2 \rightarrow O_2+H_2O_2$	67	$OH+OH \rightarrow H_2O+O$	21
$OH+O_2 \rightarrow HO_2+O$	−65	$OH+H_2 \rightarrow H_2O+H$	17
$HO_2+H_2 \rightarrow H_2O_2+H$	−2		
(2) *Reactions in solution phase*			
$OH+H_2O_2 \rightarrow H_2O+HO_2$	19	$OH+OH \rightarrow H_2O_2$	47
$OH+HO_2 \rightarrow H_2O+O_2$	77	$OH+OH \rightarrow H_2O+O$	12
$HO_2+H_2O_2 \rightarrow H_2O+OH+O_2$	30	$OH+H_2 \rightarrow H_2O+H$	18
$HO_2+HO_2 \rightarrow H_2O_2+O_2$	58		

II. Heat, Free-Energy, and Entropy Changes of Ionic Reactions involving Hydrogen Peroxide in Aqueous Solution.—(*a*) *Standard Entropies of Gaseous Radicals and Molecules.* We have taken the standard entropies [4] (S°) at 1 atmosphere pressure and 298° K. of OH (g), H_2 (g), H_2O (g), and O_2 (g) to be 43·9, 31·2, 45·1, and 49·0 e.u./mole, respectively, and have estimated a value of 50 e.u./mole for HO_2 (g) and H_2O_2 (g).

(*b*) *Heats, Entropies, and Free Energies of Gaseous Molecules and Radicals, and Related Data.* Where G° is the standard free energy of the solute gas at one atmosphere pressure and $\bar{G}^\circ$ its standard partial molal free energy in aqueous solution, then at concentrations such that $\bar{H} = \bar{H}^\circ$ we have for the free energy of hydration $\Delta G(\text{hyd.}) = \bar{G}^\circ - G^\circ = -RT \ln a$, where a is the activity of the species in solution. The entropy of hydration is calculated either from the relationship $\Delta S(\text{hyd.}) = -[\Delta G(\text{hyd.}) - \Delta H(\text{hyd.})]/T$ or, where the temperature coefficient of solubility is known, from the relationship $-\Delta S(\text{hyd.}) = \text{d}[\Delta G(\text{hyd.})]/\text{d}T$. The entropy of hydration of gaseous molecules and radicals is due almost entirely to the difference in translational entropy of the species in the gas and in the solution phase, and we have estimated the entropies of hydration of HO_2

TABLE 3

	ΔH, kcal./mole	ΔS, e.u./mole	ΔG, kcal./mole
H_2O (g) $\rightarrow H_2O$ (l)	− 10·5	− 28·4	− 2·05
H_2O_2 (g) $\rightarrow H_2O_2$ (l)	− 11·6	− 27·2	− 3·50
H_2O_2 (l) $\rightarrow H_2O_2$ (aq.)	− 0·74	8·4	− 3·24
H_2O_2 (aq.) $\rightarrow H^+$ (aq.) + HO_2^- (aq.)	8·2	− 25·7	15·8
H_2O (aq.) $\rightarrow H^+$ (aq.) + OH^- (aq.)	13·3	− 27·3	21·5
H_2 (g) $\rightarrow H_2$ (aq.)	− 1·42	− 18·8	4·18
O_2 (g) $\rightarrow O_2$ (aq.)	− 3·85	− 26·0	3·90
HO (g) $\rightarrow$ HO (aq.)	− 10	− 25	− 2·5
O_2H (g) $\rightarrow O_2H$ (aq.)	− 12	− 25	− 4·5

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[4] Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution" (Prentice-Hall, 1938).

and OH by analogy with the inert gases [5] (He, — 19 ; Ne, — 22 ; A, — 23 ; Kr, — 26 ; Xe, — 27 ; Rn, — 29 e.u.) as — 25 e.u. The heats of solution of OH and HO_2 have here been taken to be approximately — 10 and — 12 kcal./mole, respectively (cf. Table 1). The heats and entropies of solution of the monatomic halogen atoms have been assumed to approximate to those of OH. The more important values are listed in Table 3. Ionisation and vaporisation data are included here for reference.

(c) *Standard Partial Molal Entropies of Aqueous Ions.* The standard entropies $\bar{S}°$ ($\bar{S}° = \bar{S} - R \ln a$) are referred to $\bar{S}°(H^+, \text{aq.}) = 0$ at 298° K. The entropies of OH^- (aq.) and O_2H^- (aq.) may be obtained from the entropy cycles :

$$\begin{tikzcd}
H_2O\ (g) \arrow[r, "\Delta S_{i(g)}"] & H^+\ (g) + OH^-\ (g) \arrow[dd, "\begin{array}{l}\Delta S_h(H^+)\\ +\Delta S_h(OH^-)\end{array}"] \\
H_2O\ (l) \arrow[u, "\Delta S_v"] & \\
H_2O\ (aq.) \arrow[u, "-\Delta S_d"] \arrow[r, "\Delta S_{i(aq.)}"'] & H^+\ (aq.) + OH^-\ (aq.)
\end{tikzcd}$$

$$\begin{tikzcd}
H_2O_2\ (g) \arrow[r, "\Delta S_{i(g)}"] & H^+\ (g) + HO_2^-\ (g) \arrow[dd, "\begin{array}{l}\Delta S_h\ (H^+)\\ +\Delta S_h\ (HO_2^-)\end{array}"] \\
H_2O_2\ (l) \arrow[u, "\Delta S_v"] & \\
H_2O_2\ (aq.) \arrow[u, "-\Delta S_d"] \arrow[r, "\Delta S_i\ (aq.)"'] & H^+\ (aq.) + HO_2^-\ (aq.)
\end{tikzcd}$$

whence

$$- \Delta S_d + \Delta S_v + \Delta S_{i\,(g)} + \Delta S_h\ (H^+) + \Delta S_h\ (OH^- \text{ or } HO_2^-) = \Delta S_i\ (\text{aq.}),$$

where ΔS_d, ΔS_v, $\Delta S_{i(g)}$, ΔS_h (H^+), ΔS_h (OH^-), ΔS_h (HO_2^-), and ΔS_i (aq.) are the entropy changes respectively on dilution, vaporisation, gaseous ionisation, hydration of H^+, hydration of OH^-, hydration of HO_2^-, and aqueous ionisation. For OH^-, we have

$$\begin{aligned} \Delta S_h\ (OH^-) &= - \Delta S_{i(g)} - \Delta S_h\ (H^+) - \Delta S_v + \Delta S_d + \Delta S_i\ (\text{aq.}) \\ &= - 22 + 26{\cdot}0 - 28{\cdot}4 + 8{\cdot}0 - 27{\cdot}3 = - 43{\cdot}7 \end{aligned}$$

whence

$$\bar{S}°(OH^-, \text{aq.}) = - 2{\cdot}5 \text{ e.u.}$$

In order to calculate $\bar{S}°(HO_2^-, \text{aq.})$, we require the value of $\Delta S_{i(g)}$: we have assumed that the difference between the sum of the vibrational and rotational entropies of H_2O_2 and HO_2^- is small and is approximately the same as the difference for H_2O and OH^-. We then have

$$\begin{aligned} \Delta S_h\ (HO_2^-) &= - \Delta S_{i(g)} - \Delta S_h\ (H^+) - \Delta S_v + \Delta S_d + \Delta S_i\ (\text{aq.}) \\ &= - 22 + 26{\cdot}0 - 27{\cdot}2 + 8{\cdot}4 - 25{\cdot}7 = - 40{\cdot}5 \end{aligned}$$

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[5] Eley, *Trans. Faraday Soc.*, 1939, **35**, 1283.

whence

$$\bar{S}°(HO_2^-, \text{aq.}) = 7 \text{ e.u.}$$

It is assumed that the value of $\bar{S}°$ for O_2^- (aq.) is close to that for HO_2^- (aq.).

(*d*) *Subsidiary Thermochemical Quantities.* Values of ΔH, ΔG, and ΔS for reactions involving the bi- and ter-valent Fe, Co, Cr, and V ions are given in Table 4. The corresponding values for the reaction

$$M_{(aq.)}^{2+} + H^+_{(aq.)} \longrightarrow M\ (aq.)^{3+} + \tfrac{1}{2}H_2\ (g) \quad . \quad . \quad (5)$$

which are involved have been estimated in different ways. For Fe, $\Delta H(5)$ is taken to be 11·3 kcal./mole * and $\Delta G(5)$ to be 17·8 kcal./mole.[4] The corresponding entropy change is $-$ 21·8 e.u./mole, which is in agreement with Latimer's ionic entropies (Fe^{2+}, $-$ 25·9 ; Fe^{3+}, $-$ 63·3 e.u.). The thermochemical values of $\Delta H(5)$ for Co, Cr, and V are less accurately known than are the free energies : consequently, for these ions the experimental free energies † have been employed in the calculations and the heats and entropies estimated.‡ The entropies of the aqueous ions from Zn to V may be expected to vary only by relatively small amounts : for instance, the entropies of Zn^{2+}, Cu^{2+}, Fe^{2+}, and Mn^{2+} are $-$ 25·9,[7] $-$ 26·5, $-$ 25·9, and $-$ 25·9 e.u., respectively. We consider it a good approximation to take $\Delta S(5)$ to be the same for the reactions involving Co, Cr, and V ions as for those involving Fe ions.

For the reaction

$$Cu^+ + H^+ \longrightarrow Cu^{2+} + \tfrac{1}{2}H_2 \quad . \quad . \quad . \quad . \quad (6)$$

we have used Fenwick's value [8] for ΔG (3·85 kcal./mole). From the similarity of ionic radii of Cu^+ and Na^+ it is estimated that $\Delta S_{\text{hydn.}}$ of Cu^+ is $-$ 21 e.u. ; hence $\bar{S}°[Cu^+ (aq.)] = 17$ e.u. Together with Latimer's value for $\bar{S}°[Cu^{2+} (aq.)]$, $\Delta S(6)$ is calculated to be $-$ 28 e.u. and $\Delta H(6) - 4·4$ kcal./mole. For the reaction $Fe(CN)_6^{4-} + H^+ \longrightarrow Fe(CN)_6^{3-} + \tfrac{1}{2}H_2$ we assume Kolthoff and Tomsicek's value [9] for ΔG (8·3 kcal./mole) and Bichowsky and Rossini's value for ΔH (25·1 kcal./mole). The corresponding entropy change is 56·3 e.u.

The data for the halogens, with the exception of fluorine, are taken from Bichowsky and Rossini and from Latimer (*opp. cit.*). In accordance with Evans, Warhurst, and Whittle's suggestion,[10] we have taken the

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[6] *J. Amer. Chem. Soc.*, 1944, **66**, 1573.

[7] Stokes and Stokes, *Trans. Faraday Soc.*, 1945, **41**, 688.

[8] *J. Amer. Chem. Soc.*, 1926, **48**, 860. [9] *J. Phys. Chem.*, 1935, **39**, 945. [10] *J.*, 1950, 1524.

* Calculated from the heat of the reaction Fe^{2+} (aq.) + $\tfrac{1}{2}Hg^{2+}$ (aq.) $\longrightarrow$ Fe^{3+} (aq.) + Hg (l) and the heats of formation and solution of $FeCl_3$ and $Fe(NO_3)_3$, together with the heats of formation of Fe^{2+} (aq.) and of the anions. Data from Bichowsky and Rossini.[8]

† Data from Latimer (*op. cit.*). Value for V from Jones and Colvin.[6]

‡ The heats of formation of Cr^{2+} and Cr^{3+} given by Bichowsky and Rossini lead, with the above free energies, to entropies of $-$ 37 and $-$ 93·5 e.u./g.-ion, respectively : it is assumed that the free-energy data are more reliable. Jones and Colvin (*loc. cit.*) find a difference of 0·01 v between the normal potentials at 273° and 298° for $V^{2+} \longrightarrow V^{3+} + e$ corresponding to $\Delta S(5) = -$ 9·3 e.u., but the method is not accurate enough to establish a significant difference from the entropy change in the Fe reaction.

TABLE 4.

Ionic Reactions in Aqueous Solution (298° K.)

(*a*) *Non-bond breaking*

Reaction	ΔH (kcal./mole)	ΔS (e.u.)	ΔG (kcal./mole)
OH^- and metal ions :			
$Co^{3+} + OH^- \longrightarrow Co^{2+} + OH$	21	59	3
$Fe^{3+} + OH^- \longrightarrow Fe^{2+} + OH$	44	59	27
$V^{3+} + OH^- \longrightarrow V^{2+} + OH$	68	59	51
$Cr^{3+} + OH^- \longrightarrow Cr^{2+} + OH$	72	59	54
$Cu^{2+} + OH^- \longrightarrow Cu^+ + OH$	60	65	41
$Fe(CN)_6^{3-} + OH^- \longrightarrow Fe(CN)_6^{4-} + OH$	30	− 19	36
O_2^- and metal ions :			
$Co^{3+} + O_2^- \longrightarrow Co^{2+} + O_2$	− 42	53	− 58
$Fe^{3+} + O_2^- \longrightarrow Fe^{2+} + O_2$	− 18	53	− 34
$V^{3+} + O_2^- \longrightarrow V^{2+} + O_2$	6	53	− 10
$Cr^{3+} + O_2^- \longrightarrow Cr^{2+} + O_2$	10	53	− 6
$Cu^{2+} + O_2^- \longrightarrow Cu^+ + O_2$	− 2	59	− 20
$Fe(CN)_6^{3-} + O_2^- \longrightarrow Fe(CN)_6^{4-} + O_2$	− 32	− 25	− 24
HO_2^- and metal ions :			
$Co^{3+} + HO_2^- \longrightarrow Co^{2+} + HO_2$	7	55	− 9
$Fe^{3+} + HO_2^- \longrightarrow Fe^{2+} + HO_2$	31	55	15
$V^{3+} + HO_2^- \longrightarrow V^{2+} + HO_2$	54	55	38
$Cr^{3+} + HO_2^- \longrightarrow Cr^{2+} + HO_2$	58	55	42
$Cu^{2+} + HO_2^- \longrightarrow Cu^+ + HO_2$	47	62	29
$Fe(CN)_6^{3-} + HO_2^- \longrightarrow Fe(CN)_6^{4-} + HO_2$	18	− 23	25
OH^- and halogen atoms :			
$OH + F^- \longrightarrow OH^- + F$	34	− 6	36
$OH + Cl^- \longrightarrow OH^- + Cl$	3	− 21	10
$OH + Br^- \longrightarrow OH^- + Br$	− 10	− 24	− 3
$OH + I^- \longrightarrow OH^- + I$	− 27	− 29	− 18
$OH + SH^- \longrightarrow OH^- + SH$	− 30	− 10	− 27
O_2^- and halogen atoms :			
$O_2 + F^- \longrightarrow O_2^- + F$	96	− 1	96
$O_2 + Cl^- \longrightarrow O_2^- + Cl$	66	− 14	71
$O_2 + Br^- \longrightarrow O_2^- + Br$	52	− 19	58
$O_2 + I^- \longrightarrow O_2^- + I$	36	− 23	43
$O_2 + SH^- \longrightarrow O_2^- + SH$	32	− 8	35
HO_2^- and halogen atoms :			
$HO_2 + F^- \longrightarrow HO_2^- + F$	46	− 3	47
$HO_2 + Cl^- \longrightarrow HO_2^- + Cl$	17	− 17	22
$HO_2 + Br^- \longrightarrow HO_2^- + Br$	3	− 21	9
$HO_2 + I^- \longrightarrow HO_2^- + I$	− 14	− 25	− 6
$HO_2 + SH^- \longrightarrow HO_2^- + SH$	− 17	− 10	− 14
Radical-ion transfer :			
$HO_2^- + OH \longrightarrow HO_2 + OH^-$	− 13	− 3	− 12
$O_2^- + HO_2 \longrightarrow O_2 + HO_2^-$	− 50	− 2	− 49
$O_2^- + OH \longrightarrow O_2 + OH^-$	− 62	− 5	− 61

TABLE 4 (*cont.*)

(*b*) *Bond-breaking*

Reaction	ΔH (kcal./mole)	ΔS (e.u.)	ΔG (kcal./mole)
$\frac{1}{2}H_2 + HO_2 \longrightarrow HO_2^- + H^+$	− 42	− 24	− 35
$HO_2 \longrightarrow H^+ + O_2^-$	− 3	− 18	3
$\frac{1}{2}H_2 + OH \longrightarrow OH^- + H^+$	− 55	− 28	− 47
$\frac{1}{2}H_2 + O_2 \longrightarrow O_2^- + H^+$	7	− 22	14
$HO_2^- + H_2O_2 \longrightarrow HO_2 + OH + OH^-$	36	5	35
$O_2^- + H_2O_2 \longrightarrow O_2 + OH + OH^-$	− 13	3	− 14
$H_2O_2 + \frac{1}{2}H_2 \longrightarrow OH^- + OH + H^+$	− 7	− 21	1
Oxidation of H_2O by metal ions :			
$Co^{3+} + H_2O \longrightarrow Co^{2+} + OH + H^+$	34	31	25
$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + OH + H^+$	57	31	48
$V^{3+} + H_2O \longrightarrow V^{2+} + OH + H^+$	81	31	72
$Cr^{3+} + H_2O \longrightarrow Cr^{2+} + OH + H^+$	85	31	76
$Cu^{2+} + H_2O \longrightarrow Cu^+ + OH + H^+$	74	38	62
$Fe(CN)_6^{3-} + H_2O \longrightarrow Fe(CN)_6^{4-} + OH + H^+$	43	− 46	57
Oxidation of HO_2 by metal ions :			
$Co^{3+} + HO_2 \longrightarrow Co^{2+} + H^+ + O_2$	− 45	35	− 55
$Fe^{3+} + HO_2 \longrightarrow Fe^{2+} + H^+ + O_2$	− 21	35	− 31
$V^{3+} + HO_2 \longrightarrow V^{2+} + H^+ + O_2$	3	35	− 7
$Cr^{3+} + HO_2 \longrightarrow Cr^{2+} + H^+ + O_2$	7	35	− 3
$Cu^{2+} + HO_2 \longrightarrow Cu^+ + H^+ + O_2$	− 5	41	− 17
$Fe(CN)_6^{3-} + HO_2 \longrightarrow Fe(CN)_6^{4-} + H^+ + O_2$	− 35	− 43	− 22
Oxidation of H_2O_2 by metal ions :			
$H_2O_2 + Co^{3+} \longrightarrow Co^{2+} + HO_2 + H^+$	15	28	7
$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + HO_2 + H^+$	39	28	31
$H_2O_2 + V^{3+} \longrightarrow V^{2+} + HO_2 + H^+$	63	28	55
$H_2O_2 + Cr^{3+} \longrightarrow Cr^{2+} + HO_2 + H^+$	66	28	58
$H_2O_2 + Cu^{2+} \longrightarrow Cu^+ + HO_2 + H^+$	55	35	45
$Fe(CN)_6^{3-} + H_2O_2 \longrightarrow HO_2 + H^+ + Fe(CN)_6^{4-}$	26	− 49	41
Oxidation of H_2O_2 by halogen atoms :			
$F + H_2O_2 \longrightarrow HO_2 + H^+ + F^-$	− 38	− 23	− 31
$Cl + H_2O_2 \longrightarrow HO_2 + H^+ + Cl^-$	− 9	− 9	− 6
$Br + H_2O_2 \longrightarrow HO_2 + H^+ + Br^-$	5	− 5	7
$I + H_2O_2 \longrightarrow HO_2 + H^+ + I^-$	22	0	22
$SH + H_2O_2 \longrightarrow HO_2 + H^+ + SH^-$	25	− 16	30
Reduction of H_2O_2 by metal ions :			
$Co^{2+} + H_2O_2 \longrightarrow Co^{3+} + OH + OH^-$	− 28	− 51	43
$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH + OH^-$	5	− 51	20
$V^{2+} + H_2O_2 \longrightarrow V^{3+} + OH + OH^-$	− 19	− 51	− 4
$Cr^{2+} + H_2O_2 \longrightarrow Cr^{3+} + OH + OH^-$	− 23	− 51	− 8
$Cu^+ + H_2O_2 \longrightarrow Cu^{2+} + OH + OH^-$	− 11	− 57	6
Reduction of H_2O_2 by halide ions :			
$H_2O_2 + F^- \longrightarrow OH + OH^- + F$	81	2	80
$H_2O_2 + Cl^- \longrightarrow OH + OH^- + Cl$	52	− 12	56
$H_2O_2 + Br^- \longrightarrow OH + OH^- + Br$	38	− 16	43
$H_2O_2 + I^- \longrightarrow OH + OH^- + I$	23	− 21	29
$H_2O_2 + SH^- \longrightarrow OH + OH^- + SH$	15	− 15	20

TABLE 4 (*cont.*)

(*c*) *Further ionic reactions*

Reaction	ΔH (kcal./mole)	ΔS (e.u.)	ΔG (kcal./mole)
OH and metal ions :			
$Ag^+ + OH \longrightarrow Ag^{2+} + OH^-$	− 19	− 66	1
$Ce^{3+} + OH \longrightarrow Ce^{4+} + OH^-$	− 24	− 52	− 8
$Mn^{2+} + OH \longrightarrow Mn^{3+} + OH^-$	− 28	− 59	− 10
$Fe(C_{12}H_8N_2)_3{}^{2+} + OH \longrightarrow Fe(C_{12}H_8N_2)^{3+} + OH^-$			− 19
$Mo(CN)_6{}^{4-} + OH \longrightarrow Mo(CN)_6{}^{3-} + OH^-$	− 22	19	− 28
$MnO_4{}^{2} + OH \longrightarrow MnO_4{}^- + OH^-$			− 32
$Mn(CN)_6{}^{4-} + OH \longrightarrow Mn(CN)_6{}^{3-} + OH^-$	− 44	19	− 50
$FeO_2{}^{2-} + OH \longrightarrow FeO_2{}^- + OH^-$			− 60
$Co(CN)_6{}^{4-} + OH \longrightarrow Co(CN)_6{}^{3-} + OH^-$	− 58	19	− 64
HO_2 and metal ions :			
$Ag^+ + HO_2 \longrightarrow Ag^{2+} + HO_2{}^-$	− 6	− 62	13
$Ce^{3+} + HO_2 \longrightarrow Ce^{4+} + HO_2{}^-$	− 10	− 48	4
$Mn^{2+} + HO_2 \longrightarrow Mn^{3+} + HO_2{}^-$	− 14	− 55	2
$Fe(C_{12}H_8N_2)^{2+} + HO_2 \longrightarrow Fe(C_{12}H_8N_2)^{3+} + HO_2{}^-$			− 7
$Mo(CN)_6{}^{4-} + HO_2 \longrightarrow Mo(CN)_6{}^{3-} + HO_2{}^-$	− 9	23	− 16
$MnO_4{}^{2-} + HO_2 \longrightarrow MnO_4{}^- + HO_2{}^-$			− 20
$Mn(CN)_6{}^{4-} + HO_2 \longrightarrow Mn(CN)_6{}^{3-} + HO_2{}^-$	− 31	23	− 38
$FeO_2{}^{2-} + HO_2 \longrightarrow FeO_2{}^- + HO_2{}^-$			− 49
$Co(CN)_6{}^{4-} + HO_2 \longrightarrow Co(CN)_6{}^{3-} + HO_2{}^-$	− 45	23	− 52
O_2 and metal ions :			
$Ag^+ + O_2 \longrightarrow Ag^{2+} + O_2{}^-$	44	− 60	62
$Ce^{3+} + O_2 \longrightarrow Ce^{4+} + O_2{}^-$	39	− 46	53
$Mn^{2+} + O_2 \longrightarrow Mn^{3+} + O_2{}^-$	35	− 53	51
$Fe(C_{12}H_8N_2)_3{}^{2+} + O_2 \longrightarrow Fe(C_{12}H_8N_2)_3{}^{3+} + O_2{}^-$			42
$Mo(CN)_6{}^{4-} + O_2 \longrightarrow Mo(CN)_6{}^{3-} + O_2{}^-$	40	25	33
$MnO_4{}^{2-} + O_2 \longrightarrow MnO_4{}^- + O_2{}^-$			29
$Mn(CN)_6{}^{4-} + O_2 \longrightarrow Mn(CN)_6{}^{3-} + O_2{}^-$	18	25	11
$FeO_2{}^{2-} + O_2 \longrightarrow FeO_2{}^- + O_2{}^-$			0
$Co(CN)_6{}^{4-} + O_2 \longrightarrow Co(CN)_6{}^{3-} + O_2$	4	25	− 3

(*d*) *Reactions involving ozone*

Reaction	ΔH (kcal./mole)	ΔS (e.u.)	ΔG (kcal./mole)
$O_3 + 2OH^- \longrightarrow 2O_2{}^- + H_2O$	16	6	14
$O_3 + H_2O \longrightarrow 2HO_2$	49	− 5	51
$O_3 + OH^- \longrightarrow O_2{}^- + HO_2$	33	0	33
$H_2O_2 + O_3 \longrightarrow OH + HO_2 + O_2$	19	5	18
$HO_2{}^- + O_3 \longrightarrow OH + O_2{}^- + O_2$	8	11	5
$HO_2 + O_3 \longrightarrow OH + 2O_2$	− 42	9	− 45
$OH + O_3 \longrightarrow HO_2 + O_2$	− 31	− 2	− 30
$Co^{2+} + O_3 + H_2O \longrightarrow Co^{3+} + OH^- + O_2 + OH$	15	− 52	31
$O_3 + H_2O \longrightarrow H_2O_2 + O_2$	− 10	− 1	− 10
$(HO_2 + Co^{3+} + OH^- \longrightarrow Co^{2+} + H_2O + O_2$	− 58	61	− 76)

dissociation energy of fluorine to be 42 kcal./mole (mean value). Values calculated for reactions involving SH are very approximate: these employ West's estimate [11] of the electron affinity of SH, and it is assumed that $D(S_2) = 83$ kcal./mole.*

(*e*) *Heat and Free Energy of Formation of* O_2^-. We have estimated the heat of hydration of O_2^- to be 63 kcal./g.-ion, relative to the value 282 kcal. for H^+. The small difference between this and a previous estimate [2] is due to the fact that in the present calculations we have, following the method of Eley and Evans,[12] taken account of small effects on the reorientation energy of the co-ordinated water molecules in the first hydration shell and on the energy of Born charging caused by the asymmetry of the ion. Together with the electron affinity of O_2 calculated from the lattice energies of peroxides (16 kcal.), this yields:

	ΔH	ΔS	ΔG
$O_2\text{ (aq.)} + \tfrac{1}{2}H_2\text{ (g)} \longrightarrow O_2^-\text{ (aq.)} + H^+\text{ (aq.)}$	7	− 31	16

The value of ΔG for this reaction, in conjunction with our data for HO_2, correspond to a free energy of ionisation of HO_2 of ~ 3 kcal./mole. This agrees well with the results in the iron catalysis of hydrogen peroxide decomposition obtained by Barb, Baxendale, George, and Hargrave,[13] and by Weiss and Humphrey.[14] With the above value, HO_2 would be dissociated to the extent of approximately 50% at pH 2, whereas at pH 0 the ratio $O_2^- : HO_2$ would be approximately 1 : 100. The hydrogen-ion dependence of the consumption ratio $\Delta H_2O_2/\Delta Fe^{2+}$ in the catalytic burst at the start of the reaction can thus be well accounted for.†

(*f*) *Reactions involving Ozone.* A number of schemes have been suggested for reactions of ozone involving radicals and ions of the type we have been considering (cf. Taube and Bray [16]). Coupling the heat and free-energy change of $O_3 \longrightarrow O_2 + O$ with the data already provided, we obtain the thermodynamic quantities in Table 4(*d*) for several of the reactions which have been discussed. These reactions are certainly composite and do not necessarily represent the primary steps. The thermodynamic quantities may be helpful in the elucidation of the reaction mechanisms.

Hill [17] has postulated that the Co^{2+}-catalysed decomposition of ozone involves the $[Co(OH)]^{2+}$ ion-pair complex. Some approximate quantities involving this complex and O_3 are included in Table 4(*d*), it having been assumed that the energetics of the reaction $Co^{3+} + OH^- \longrightarrow [Co(OH)]^{2+}$ are the same as those of the corresponding Fe^{3+} reaction.

(*g*) *Standard Oxidation–Reduction Potentials.* A number of estimates have been made of the oxidation–reduction potentials of the O_2/O_2^-,

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[11] *J. Phys. Chem.*, 1935, **39**, 493.
[12] *Trans. Faraday Soc.*, 1938, **34**, 1093.
[13] *Nature*, 1949, **163**, 692.
[14] *Ibid.*, p. 691.
[15] *J. Amer. Chem. Soc.*, 1942, **64**, 2468.
[16] *Ibid.*, 1940, **62**, 3357.
[17] *Ibid.*, 1948, **70**, 1306.

* In calculating the values listed in Table 4(*c*) we have used the free-energy data given in Latimer's compilation,[4] and in some cases the tonic entropies have been estimated.

† A value of 10^{-2} for the dissociation constant of HO_2 has been independently postulated by Taube.[15]

OH/OH^- and HO_2/HO_2^- systems, the best-known of which are those contained in Latimer's monograph.[4] Since the publication of the latter (1938), a number of thermodynamic quantities relating to these potentials have been revised.* On the basis of data here proposed, the standard potentials (to the nearest 0·1 v) of these systems at 25° c. are as follows:

	E_0 (volts against N.H.E.)
$OH\ (aq.) + e \rightarrow OH^-\ (aq.)$	2·0
$HO_2\ (aq.) + e \rightarrow HO_2^-\ (aq.)$	1·5
$O_2\ (aq.) + e \rightarrow O_2^-\ (aq.)$	− 0·6

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[18] Present communication.

* Our value for the $H....O_2$ bond-dissociation energy is within the limits of accuracy of a recent estimate by Robertson[18] based on the appearance potential.