AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

POTENTIAL - pH DIAGRAMS AT TEMPERATURES ABOVE 298.16°K
PART 2. POTENTIAL-pH DIAGRAMS OF WATER FOR THE TEMPERATURE RANGE 298.16 - 573.16°K

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R.T. LOWSON

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ABSTRACT

The Potential – pH diagrams are presented for water over the temperature range 298.16 – 573.16°K. The diagrams are discussed with reference to variation of the thermodynamic stability of species $H_2O_{(\ell)}$, H^+, OH^-, H^-, H_2O_2, HO_2^-, H_1, H_2, O_2, O_3 and $H_2O_{(g)}$ with temperature. The diagrams demonstrate the variation of K_w and the neutral point of water with temperature. The maximum for K_w was -11.86 at 473.16°K (200°C) with a corresponding minimum pH value of 5.93.

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CONTENTS (continued)

1. INTRODUCTION

This report presents the Potential – pH diagrams of water for the temperature range 298–573 °K (25–300 °C) using the thermodynamic data for water along its saturation vapour pressure curve. The theoretical background for deriving the diagrams and the thermodynamic data at elevated temperatures forms Part 1 of this series, (Lowson 1971). The presentation of the data and diagrams follows that of Pourbaix (1966).

2. SUBSTANCES CONSIDERED AND THEIR THERMODYNAMIC DATA

The substances considered and their thermodynamic data at elevated temperatures are listed below. The data sources have been collated separately.

The method for obtaining $\Delta \overline{G}^\circ_f$ (T) by integration is outlined in Part 1.

PARTIAL MOLAL GIBBS ENERGIES OF FORMATION OF THE SUBSTANCES CONSIDERED

°K			298.16	323.16	373.16	423.16	473.16	523.16	573.16
°C			25	50	100	150	200	250	300
$H_2O_{(\ell)}$	liquid	Water	-56687	-55745	-53889	-52275	-50718	-49256	-47898
H^+	aqueous	Hydrogen Ion	standard state 0 for all temperatures						
OH^-	aqueous	Hydroxide Ion	-37590	-36090	-32810	-29120	-25030	-20540	-15640
H^-	aqueous	Hydride Ion	51900	51850	51890	52120	52520	53110	53879
H_2O_2	aqueous	Hydrogen Peroxide	-32050	-30887	-28456	-25878	-23154	-20286	-17255
HO_2^-	aqueous	Hydrogen Peroxide Ion	-16100	-14243	-10532	- 5763	- 3157	509	4670
H_1	gas	Atomic Hydrogen	48581	48281	47658	46991	46300	45583	44893
H_2	gas	Natural Hydrogen	standard state 0 for all temperatures						
O_2	gas	Natural Oxygen	standard state 0 for all temperatures						
O_3	gas	Ozone	39000	40640	43900	47067	50195	53256	56263
$H_2O_{(g)}$	gas	Water	-54639	-54372	-53827	-53259	-52682	-52092	-51492

Reported as cal mole^{-1}

Data Sources

Water, Liquid

$\bar{C}_p$ = $51.99 - 0.1676T + 0.2081\ T^2$ cal. mole^{-1} deg^{-1} range 298.16–573.16 °K (Khodakovskiy et al. 1968)

$\Delta\bar{H}_f$ (298.16) = -68315 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}_f$ (298.16) = -56687 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}_f$ (T) = $-78204.4 - 51.99\ T\ \ell n\ T + 346.5T + 0.083805T^2 - 0.03468 \times 10^{-3}\ T^3$ cal. mole^{-1} Obtained by integration

Hydrogen Ion, Aqueous

$\Delta\bar{G}_f$ (T) = 0 By definition

Hydroxide Ion, Aqueous

$\Delta\bar{G}_f$ (T) = $-19957.0 + 200.96T\ \ell n\ T - 1102.2T - 0.3970T^2 + 0.0001856T^3$ cal. mole^{-1} Fitted by computer to data quoted by Khodakovskiy et al. (1968)

Hydride Ion, Aqueous

$\bar{C}^\circ_{P_2}$ = $-0.0728T$ cal. mole^{-1} deg^{-1} empirical equation (Lowson 1971, Khodakovskiy 1969)

$\Delta\bar{H}_f$ (298.16) = 52740 cal. mole^{-1} estimated

$\bar{S}$ (298.16) = -2.82 e.u. empirical equation (Lowson 1971, Powell & Latimer 1951, Laidler 1956)

$\Delta\bar{G}^\circ_f$ (298.16) = 51900 cal. mole^{-1} (Latimer 1952)

$\Delta\bar{G}^\circ_f$ (T) = $55976 - 24.5T + 0.0364T^2$ cal. mole^{-1} Obtained by integration

Hydrogen Peroxide, Aqueous

$\bar{C}^\circ_{P_2}$ = $0.0581T$ cal. mole^{-1} deg^{-1} empirical equation (Lowson 1971, Khodakovskiy 1969)

$\Delta\bar{H}^\circ_f$ (298.16) = -45690 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (298.16) = -32050 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (T) = $-43108 + 28.4T + 0.02905T^2$ cal. mole^{-1} Obtained by integration

Hydrogen Peroxide Ion, Aqueous

$\bar{C}^\circ_{P_2}$ = $0.0060T$ cal. mole^{-1} deg^{-1} empirical equation (Lowson 1971, Khodakovskiy 1969)

$\Delta\bar{H}^\circ_f$ (298.16) = -38320 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (298.16) = -16100 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (T) = $-38586.7 + 76.3T - 0.003T^2$ cal. mole^{-1} Obtained by integration

Atomic Hydrogen, Gas

$\bar{C}_p$ = 4.9681 cal. mole^{-1} deg^{-1} range 298.16 – 573.16 °K (McBride et al. 1963)

$\Delta\bar{H}^\circ_f$ (298.16) = 52095 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (298.16) = 48581 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (T) = $50614 - 4.968T \ell n\, T + 21.49T$ cal. mole^{-1} Obtained by integration

Hydrogen, Gas

$\Delta\bar{G}^\circ_f$ (T) = 0 By definition

Oxygen, Gas

$\Delta\bar{G}^\circ_f$ (T) = 0 By definition

Ozone, Gas

$\bar{C}_p$ = $11.23 + 1.92 \times 10^{-3}\, T - 2.16 \times 10^5\, T^{-2}$ cal mole^{-1} deg^{-1} range 298.16 – 573.16 °K (Kelley 1960)

$\Delta\bar{H}^\circ_f$ (298.16) = 34100 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (298.16) = 39000 cal. mole^{-1} (Wagman et al. 1968)

$\Delta\bar{G}^\circ_f$ (T) = $14971 - 11.23T \ell n\, T + 1.08 \times 10^5\, T^{-1} + 143.6T - 0.96 \times 10^{-3}\, T^2$ cal. mole^{-1} Obtained by integration

Water, Gas

$\Delta\bar{G}^\circ_f$ (T) = $-56930 + 2.9309T \ell n\, T - 0.08 \times 10^5\, T^{-1} - 8.74T - 0.64 \times 10^{-3}\, T^2$ cal. mole^{-1} (Weast 1969)

3. REACTIONS AND EQUILIBRIUM FORMULAE

3.1 Two Dissolved Species

Relative stability of H^+, OH^-, H^-, H_2O_2 and HO_2^-

Equations 1 and 1' $H_2O_{(\ell)} = OH^- + H^+$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H^+/OH^-
298.16	Log $(OH^-) = -14.00 + pH$	$pH = 7.00$
323.16	$= -13.29 + pH$	$= 6.64$
373.16	$= -12.34 + pH$	$= 6.17$
423.16	$= -11.96 + pH$	$= 5.98$
473.16	$= -11.86 + pH$	$= 5.93$
523.16	$= -12.00 + pH$	$= 6.00$
573.16	$= -12.30 + pH$	$= 6.15$

Equations 2 and 2' $H_2O_2 = HO_2^- + H^+$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H_2O_2/HO_2^-
298.16	$\log \frac{(HO_2^-)}{(H_2O_2)} = -11.69$	pH $= 11.69$
323.16	$= -11.26$	$= 11.26$
373.16	$= -10.50$	$= 10.50$
423.16	$= -10.39$	$= 10.39$
473.16	$= -9.24$	$= 9.24$
523.16	$= -8.69$	$= 8.69$
573.16	$= -8.36$	$= 8.36$

Equations 3 and 3' $H^- = H^+ + 2e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H^-/H^+
298.16	$E_o = -1.125 + 0.0296 \log (H^+/H^-)$	$E_o = -1.125$
323.16	$= -1.124 + 0.0321 \log (H^+/H^-)$	$= -1.124$
373.16	$= -1.125 + 0.0370 \log (H^+/H^-)$	$= -1.125$
423.16	$= -1.130 + 0.0420 \log (H^+/H^-)$	$= -1.130$
473.16	$= -1.139 + 0.0469 \log (H^+/H^-)$	$= -1.139$
523.16	$= -1.152 + 0.0519 \log (H^+/H^-)$	$= -1.152$
573.16	$= -1.168 + 0.0569 \log (H^+/H^-)$	$= -1.168$

Equations 4 and 4' $H^- + H_2O_{(\ell)} = OH^- + 2H^+ + 2e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H^-/OH^-
298.16	$E_o = -0.711 - 0.0592\,\text{pH} + 0.0296 \log (OH^-/H^-)$	$E_o = -0.711 - 0.0592\,\text{pH}$
323.16	$= -0.698 - 0.0641\,\text{pH} + 0.0321 \log (OH^-/H^-)$	$= -0.698 - 0.0641\,\text{pH}$
373.16	$= -0.668 - 0.0740\,\text{pH} + 0.0370 \log (OH^-/H^-)$	$= -0.668 - 0.0740\,\text{pH}$
423.16	$= -0.628 - 0.0840\,\text{pH} + 0.0420 \log (OH^-/H^-)$	$= -0.628 - 0.0840\,\text{pH}$
473.16	$= -0.582 - 0.0939\,\text{pH} + 0.0469 \log (OH^-/H^-)$	$= -0.582 - 0.0939\,\text{pH}$
523.16	$= -0.529 - 0.1038\,\text{pH} + 0.0519 \log (OH^-/H^-)$	$= -0.529 - 0.1038\,\text{pH}$
573.16	$= -0.469 - 0.1137\,\text{pH} + 0.0569 \log (OH^-/H^-)$	$= -0.469 - 0.1137\,\text{pH}$

Equations 5 and 5' $2H_2O_{(\ell)} = H_2O_2 + 2H^+ + 2e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H^+/H_2O_2
298.16	$E_o = 1.763 - 0.0592\ pH + 0.0296\ Log\ (H_2O_2)$	$E_o = 1.763 - 0.0888\ pH$
323.16	$= 1.748 - 0.0641\ pH + 0.0321\ Log\ (H_2O_2)$	$= 1.748 - 0.0962\ pH$
373.16	$= 1.720 - 0.0740\ pH + 0.0370\ Log\ (H_2O_2)$	$= 1.720 - 0.1110\ pH$
423.16	$= 1.706 - 0.0840\ pH + 0.0420\ Log\ (H_2O_2)$	$= 1.706 - 0.1260\ pH$
473.16	$= 1.697 - 0.0939\ pH + 0.0469\ Log\ (H_2O_2)$	$= 1.697 - 0.1308\ pH$
523.16	$= 1.696 - 0.1038\ pH + 0.0519\ Log\ (H_2O_2)$	$= 1.696 - 0.1557\ pH$
573.16	$= 1.703 - 0.1137\ pH + 0.0569\ Log\ (H_2O_2)$	$= 1.703 - 0.1646\ pH$

Equations 6 and 6' $2H_2O_{(\ell)} = HO_2^- + 3H^+ + 2e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H^+/HO_2^-
298.16	$E_o = 2.109 - 0.0887\ pH + 0.0296\ Log\ (HO_2^-)$	$E_o = 2.109 - 0.1183\ pH$
323.16	$= 2.109 - 0.0962\ pH + 0.0321\ Log\ (HO_2^-)$	$= 2.109 - 0.1283\ pH$
373.16	$= 2.109 - 0.1111\ pH + 0.0370\ Log\ (HO_2^-)$	$= 2.109 - 0.1481\ pH$
423.16	$= 2.142 - 0.1260\ pH + 0.0420\ Log\ (HO_2^-)$	$= 2.142 - 0.1680\ pH$
473.16	$= 2.131 - 0.1408\ pH + 0.0469\ Log\ (HO_2^-)$	$= 2.131 - 0.1877\ pH$
523.16	$= 2.147 - 0.1557\ pH + 0.0519\ Log\ (HO_2^-)$	$= 2.147 - 0.2076\ pH$
573.16	$= 2.178 - 0.1706\ pH + 0.0569\ Log\ (HO_2^-)$	$= 2.178 - 0.2275\ pH$

Equations 7 and 7' $OH^- + H_2O_{(\ell)} = H_2O_2 + H^+ + 2e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for OH^-/H_2O
298.16	$E_o = 1.349 - 0.0296\ pH + 0.0296\ Log\ (H_2O_2/OH^-)$	$E_o = 1.349 - 0.0296\ pH$
323.16	$= 1.322 - 0.0321\ pH + 0.0321\ Log\ (H_2O_2/OH^-)$	$= 1.322 - 0.0321\ pH$
373.16	$= 1.263 - 0.0370\ pH + 0.0370\ Log\ (H_2O_2/OH^-)$	$= 1.263 - 0.0370\ pH$
423.16	$= 1.204 - 0.0420\ pH + 0.0420\ Log\ (H_2O_2/OH^-)$	$= 1.204 - 0.0420\ pH$
473.16	$= 1.140 - 0.0469\ pH + 0.0469\ Log\ (H_2O_2/OH^-)$	$= 1.140 - 0.0469\ pH$
523.16	$= 1.074 - 0.0519\ pH + 0.0519\ Log\ (H_2O_2/OH^-)$	$= 1.074 - 0.0519\ pH$
573.16	$= 1.003 - 0.0569\ pH + 0.0569\ Log\ (H_2O_2/OH^-)$	$= 1.003 - 0.0569\ pH$

Equations 8 and 8' $OH^- + H_2O_{(\ell)} = HO_2^- + 2H^+ + 2e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for OH^-/OH_2^-
298.16	$E_o = 1.695 - 0.0592\ pH + 0.0296\ Log\ (HO_2^-/OH^-)$	$E_o = 1.695 - 0.0592\ pH$
323.16	$= 1.682 - 0.0641\ pH + 0.0321\ Log\ (HO_2^-/OH^-)$	$= 1.682 - 0.0641\ pH$
373.16	$= 1.651 - 0.0740\ pH + 0.0370\ Log\ (HO_2^-/OH^-)$	$= 1.651 - 0.0740\ pH$
423.16	$= 1.640 - 0.0840\ pH + 0.0420\ Log\ (HO_2^-/OH^-)$	$= 1.640 - 0.0840\ pH$
473.16	$= 1.574 - 0.0939\ pH + 0.0469\ Log\ (HO_2^-/OH^-)$	$= 1.574 - 0.0939\ pH$
523.16	$= 1.524 - 0.1038\ pH + 0.0519\ Log\ (HO_2^-/OH^-)$	$= 1.524 - 0.1038\ pH$
573.16	$= 1.479 - 0.1137\ pH + 0.0569\ Log\ (HO_2^-/OH^-)$	$= 1.479 - 0.1137\ pH$

3.2 Two Gaseous Substances

Relative stability of H_1, H_2, O_2 and O_3

Equations 9 and 9' $H_2 = H_1 + H^+ + e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H_2/H_1
298.16	$E_o = 2.107 - 0.0592\ pH + 0.0592\ Log\ (p_{H_1}/p_{H_2})$	$E_o = 2.107 - 0.0592\ pH$
323.16	$= 2.094 - 0.0641\ pH + 0.0641\ Log\ (p_{H_1}/p_{H_2})$	$= 2.094 - 0.0641\ pH$
373.16	$= 2.067 - 0.0740\ pH + 0.0740\ Log (p_{H_1}/p_{H_2})$	$= 2.067 - 0.0740\ pH$
423.16	$= 2.038 - 0.0840\ pH + 0.0840\ Log\ (p_{H_1}/p_{H_2})$	$= 2.038 - 0.0840\ pH$
473.16	$= 2.008 - 0.0939\ pH + 0.0939\ Log\ (p_{H_1}/p_{H_2})$	$= 2.008 - 0.0939\ pH$
523.16	$= 1.997 - 0.1038\ pH + 0.1038\ Log\ (p_{H_1}/p_{H_2})$	$= 1.997 - 0.1038\ pH$
573.16	$= 1.945 - 0.1137\ pH + 0.1137\ Log\ (p_{H_1}/p_{H_2})$	$= 1.945 - 0.1137\ pH$

Equations 10 and 10' $H_2 + 2H_2O_{(\ell)} = O_2 + 6H^+ + 6e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for H_2/O_2
298.16	$E_o = 0.819 - 0.0592\ pH + 0.0099\ Log\ (p_{O_2}/p_{H_2})$	$E_o = 0.819 - 0.0592\ pH$
323.16	$= 0.806 - 0.0641\ pH + 0.0107\ Log\ (p_{O_2}/p_{H_2})$	$= 0.806 - 0.0641\ pH$
373.16	$= 0.779 - 0.0740\ pH + 0.0123\ Log\ (p_{O_2}/p_{H_2})$	$= 0.779 - 0.0740\ pH$
423.16	$= 0.756 - 0.0840\ pH + 0.0140\ Log\ (p_{O_2}/p_{H_2})$	$= 0.756 - 0.0840\ pH$
473.16	$= 0.733 - 0.0939\ pH + 0.0156\ Log\ (p_{O_2}/p_{H_2})$	$= 0.733 - 0.0939\ pH$
523.16	$= 0.712 - 0.1038\ pH + 0.0173\ Log\ (p_{O_2}/p_{H_2})$	$= 0.712 - 0.1038\ pH$
573.16	$= 0.692 - 0.1137\ pH + 0.0190\ Log\ (p_{O_2}/p_{H_2})$	$= 0.692 - 0.1137\ pH$

Equations 11 and 11' $O_2 + H_2O_{(\ell)} = O_3 + 2H^+ + 2e^-$

Temp. °K	Relative Stability	Limit of domain of relative predominance for O_2/O_3
298.16	$E_0 = 2.075 - 0.0592\,pH + 0.0296\,Log\,(p_{O_3}/p_{O_2})$	$E_0 = 2.075 - 0.0592\,pH$
323.16	$= 2.090 - 0.0641\,pH + 0.0321\,Log\,(p_{O_3}/p_{O_2})$	$= 2.090 - 0.0641\,pH$
373.16	$= 2.120 - 0.0740\,pH + 0.0370\,Log\,(p_{O_3}/p_{O_2})$	$= 2.120 - 0.0740\,pH$
423.16	$= 2.154 - 0.0840\,pH + 0.0420\,Log\,(p_{O_3}/p_{O_2})$	$= 2.154 - 0.0840\,pH$
473.16	$= 2.188 - 0.0939\,pH + 0.0469\,Log\,(p_{O_3}/p_{O_2})$	$= 2.188 - 0.0939\,pH$
523.16	$= 2.223 - 0.1038\,pH + 0.0519\,Log\,(p_{O_3}/p_{O_2})$	$= 2.223 - 0.1038\,pH$
573.16	$= 2.258 - 0.1137\,pH + 0.0569\,Log\,(p_{O_3}/p_{O_2})$	$= 2.258 - 0.1137\,pH$

3.3 One Dissolved Substance and One Gaseous Substance

Equation 12 $H_2O_{(\ell)} = H_2O_{(g)}$

Temp. °K	Stability of Gaseous Substance
298.16	$Log\,p_{H_2O} = -1.591$
323.16	$= -0.928$
373.16	$= -0.036$
423.16	$= 0.508$
473.16	$= 0.907$
523.16	$= 1.185$
573.16	$= 1.371$

Equation 13 $H_1 = H^+ + e^-$

Temp. °K	Stability of Gaseous Substance
298.16	$E_0 = -2.107 - 0.0592\,pH - 0.0592\,Log\,p_{H_1}$
323.16	$= -2.094 - 0.0641\,pH - 0.0641\,Log\,p_{H_1}$
373.16	$= -2.067 - 0.0740\,pH - 0.0740\,Log\,p_{H_1}$
423.16	$= -2.038 - 0.0840\,pH - 0.0840\,Log\,p_{H_1}$
473.16	$= -2.008 - 0.0939\,pH - 0.0939\,Log\,p_{H_1}$
523.16	$= -1.977 - 0.1038\,pH - 0.1038\,Log\,p_{H_1}$
573.16	$= -1.945 - 0.1137\,pH - 0.1137\,Log\,p_{H_1}$

Equation 14 and equation (a) $H_2 = 2H^+ + 2e^-$

Temp. °K	Stability of Gaseous Substance	Equation (a) Partial Pressure of H_2, 1 atmosphere at temperature T
298.16	$E_o = 0.000 - 0.0592\ pH - 0.0296\ Log\ p_{H_2}$	$E_o = 0.000 - 0.0592\ pH$
323.16	$= 0.000 - 0.0641\ pH - 0.0321\ Log\ p_{H_2}$	$= 0.000 - 0.0641\ pH$
373.16	$= 0.000 - 0.0740\ pH - 0.0370\ Log\ p_{H_2}$	$= 0.000 - 0.0740\ pH$
423.16	$= 0.000 - 0.0840\ pH - 0.0420\ Log\ p_{H_2}$	$= 0.000 - 0.0840\ pH$
473.16	$= 0.000 - 0.0939\ pH - 0.0469\ Log\ p_{H_2}$	$= 0.000 - 0.0939\ pH$
523.16	$= 0.000 - 0.1038\ pH - 0.0519\ Log\ p_{H_2}$	$= 0.000 - 0.1038\ pH$
573.16	$= 0.000 - 0.1137\ pH - 0.0569\ Log\ p_{H_2}$	$= 0.000 - 0.1137\ pH$

Equation 15 and equation (b) $2H_2O_{(\ell)} = O_2 + 4H^+ + 4e^-$

Temp. °K	Stability of Gaseous Substance	Equation (b) Partial Pressure of O_2, 1 atmosphere at temperature T
298.16	$E_o = 1.229 - 0.0592\ pH + 0.0148\ Log\ p_{O_2}$	$E_o = 1.229 - 0.0592\ pH$
323.16	$= 1.209 - 0.0641\ pH + 0.0160\ Log\ p_{O_2}$	$= 1.209 - 0.0641\ pH$
373.16	$= 1.168 - 0.0740\ pH + 0.0185\ Log\ p_{O_2}$	$= 1.168 - 0.0740\ pH$
423.16	$= 1.133 - 0.0840\ pH + 0.0210\ Log\ p_{O_2}$	$= 1.133 - 0.0840\ pH$
473.16	$= 1.100 - 0.0939\ pH + 0.0235\ Log\ p_{O_2}$	$= 1.100 - 0.0939\ pH$
523.16	$= 1.068 - 0.1038\ pH + 0.0260\ Log\ p_{O_2}$	$= 1.068 - 0.1038\ pH$
573.16	$= 1.038 - 0.1137\ pH + 0.0284\ Log\ p_{O_2}$	$= 1.038 - 0.1137\ pH$

Equation 16 $3H_2O_{(\ell)} = O_3 + 6H^+ + 6e^-$

Temp. °K	Stability of Gaseous Substance
298.16	$E_o = 1.511 - 0.0592\ pH + 0.0099\ Log\ p_{O_3}$
323.16	$= 1.502 - 0.0641\ pH + 0.0107\ Log\ p_{O_3}$
373.16	$= 1.486 - 0.0740\ pH + 0.0123\ Log\ p_{O_3}$
423.16	$= 1.474 - 0.0840\ pH + 0.0140\ Log\ p_{O_3}$
473.16	$= 1.462 - 0.0939\ pH + 0.0156\ Log\ p_{O_3}$
523.16	$= 1.453 - 0.1038\ pH + 0.0173\ Log\ p_{O_3}$
573.16	$= 1.445 - 0.1137\ pH + 0.0190\ Log\ p_{O_3}$

4. EQUILIBRIUM DIAGRAMS AND THEIR INTERPRETATION

4.1 Establishment of the Diagrams

Equation 14 expresses the reduction equilibrium of water according to the reaction $H_2 = 2H^+ + 2e^-$ and Equation 15 the oxidation equilibrium according to the reaction $2H_2O = O_2 + 4H^+ + 4e^-$. By setting the partial pressure of hydrogen or oxygen to 1 atmosphere, we obtained equations (a) and (b) respectively. These equations have been plotted in Figures 1 a – g.

It follows that below line (a) water decomposes to hydrogen and above line (b) water decomposes to oxygen under the defined pressure conditions. The area between lines (a) and (b) delineates the region of thermodynamic stability of water. Because of their fundamental importance in demonstrating the properties of an aqueous system, lines (a) and (b) are included on all potential – pH diagrams.

Equations 1' to 5', 7' and 8' have been plotted in Figures 2 a – g for each temperature considered. These figures illustrate those areas in which a particular ion or neutral molecule is the dominant species. Each area is called a domain of relative predominance and the species considered were H^-, H^+, OH^-, H_2O_2, and HO_2^-. Similarly, the domains of relative predominance of the gases H_2, O_2, and O_3 (note that no domain of predominance exists for H_1) at each temperature considered are represented in Figures 3 a – g using Equations 10 and 11.

4.2 Thermodynamic Stability of Water

Water may be considered to decompose from two points of view: (i) by the more familiar acid-base decomposition into the ions H^+ and OH^-

$$H_2O_{(\ell)} = H^+ + OH^- \qquad (1)$$

and (ii) by the less familiar redox decomposition to the gases H_2 and O_2

$$2H_2O_{(\ell)} = 2H_{2(g)} + O_{2(g)} \qquad (17)$$

Equation 1 described the relative stability of the acid-base reaction and demonstrated that along the saturation vapour pressure curve ionisation increases with temperature to a maximum value at about 473.16°K after which the degree of ionisation decreases. Equation 1' defines the neutral point where $(H^+) = (OH^-)$. The hydrogen ion concentration is more commonly expressed by its negative logarithm known as the pH, that is $pH = -\log H^+$, and at the neutral point at 298.16°K $pH = 7$. The change in ionisation with temperature causes the hydrogen ion concentration to pass through a maximum value at 473.16°K and, therefore, the pH of the neutral point will drop to a minimum value of 5.93 at 473.16°K before rising again.

The alternative redox point of view, Equation 17, is the sum of two half-cell reactions: the reduction of the hydrogen ion to gaseous hydrogen according to Equation 14, and the oxidation of the combined oxygen of the water to gaseous oxygen according to Equation 15. By combining these two half-cell reactions we obtain Equation 17. Then from Equation 17 we may equally well define a neutral point for water as

$$p_{H_2} = 2\,p_{O_2}$$

In the same way that pH was defined as $-\log H^+$, we may define the hydrogen and oxygen partial pressures as

$$rH = -\log p_{H_2} \text{ and } rO = -\log p_{O_2}$$

hence at the neutral point

$$rH = rO - 0.3010 \quad . \qquad (18)$$

At the neutral point the potential of the two half-cell reactions will be equal and we may, therefore, define the potential of the neutral point, $E_{o(n)}$, as

$$E_{o(n)} = E_{o(14)} = E_{o(15)} \qquad (19)$$

By combining Equations 14, 15, 18 and 19 we may solve for $E_{o(n)}$ and evaluate rH and rO. The following results are obtained.

Temp °K	$E_{o(n)}$	rH	rO
		at the neutral point	
298 16	$E_o = 0.816 - 0.0592$ pH	27.567	27.868
323 16	$= 0\ 803 - 0\ 0641$ pH	25.009	25.310
373 16	$= 0.775 - 0.0740$ pH	20.939	21.240
423 16	$= 0\ 751 - 0.0840$ pH	17.883	18.180
473 16	$= 0\ 729 - 0\ 0939$ pH	15.535	15.836
523 16	$= 0\ 707 - 0.1038$ pH	13.618	13.919
573 16	$= 0\ 696 - 0\ 1137$ pH	11 667	11.968

Note: Equations 10 10' defined the domains of predominance of H_2 and O_2. Equation 10' does not define the neutral point since it requires rH = rO whereas the neutral point is defined by equation 18. This accounts for the slight difference in values between $E_{o(10')}$ and $E_{o(n)}$

These rH and rO values have been plotted in Figures 4 a – g and illustrate the progressive loss of thermodynamic stability with increasing temperature. Figure 5 is a graph of the rH values at the neutral point plotted against temperature. The extrapolated value at rH = O was obtained using a computer to fit the results to the general equation $a + bT + cT^2$. The critical temperature and pressure of water is 647.16°K (374°C) and 219.5 atm. (222.1 bars) (Weast 1969) and since its variation of thermodynamic stability with temperature may change above this point the extrapolation can no longer be considered valid past this point. However, as a general conclusion it may be said that in measuring the physical properties of water above 873 16°K at relatively low pressures the presence of other gases should be taken into account.

4 3 The Effect of Temperature for Particular Species

4 3 1 Reducing species, hydrogen and the hydride ion

The reduction of water to monatomic gaseous hydrogen, H_1, will only occur to any appreciable extent at the very low electrode potential of ~ – 2.0 V. The exact values are given by Equation 13 and it can be seen that the effect of temperature at low pH is minimal but the reaction becomes increasingly pH and concentration dependent with increasing temperature. Under the normal conditions such as brought about by the impressed potential of a corroding metal (iron corrodes in a solution of 1N sulphuric acid at a potential of ~ –0.25 V) the monatomic gaseous hydrogen concentration would be very low (approximately 1×10^{-20} atm.).. However, the electrode potential for an alkaline metal reacting with water (Li, Na, K, Rb, Cs) would be at this low potential and evolution of monatomic gaseous hydrogen, or nascent hydrogen, is to be expected.

The monatomic gaseous hydrogen, H_1, is also in equilibrium with the diatomic species H_2 according to Equation 9. The monatomic species will predominate above 2.0 V. However, at this high voltage the equilibrium partial pressures of these gases are so small (1×10^{-70} atm.) that the concentration has no practical interest.

The hydride ion, H^-, will be the predominant dissolved species below the lines corresponding to Equations 3' and 4'. These are at relatively low potentials but such conditions will occur in the presence of alkali metals or with an impressed voltage. Because Equation 4' becomes increasingly dependent on pH with increasing temperature, the domain of predominance for the hydride ion tends to be foreshortened at higher pH with increasing temperature to the advantage of the OH^- ion.

Reduction of water to diatomic gaseous hydrogen, H_2, will tend to occur with any metal whose potential is below line (a). Between lines (a) and (b) water is considered to be thermodynamically stable while above line (b) water may be oxidised by an oxidant such as fluorine to oxygen. The equilibrium line between reducing to hydrogen gas or oxidising to oxygen gas is 10'. With increasing temperature the equations of lines (a), (b) and 10' become increasingly pH dependent, the lines pivot around their values at pH = 0. The sum effect is that at low pH temperature has little effect on changing the reduction or oxidation of water, while at high pH the solutions become increasingly oxidisable with increasing temperature.

The effect of temperature on the concentration of the hydrogen ion H^+ and hydroxide ion OH^- and their inter-relationship is discussed in Section 4.4. In the context of the present needs it may be said that with increasing temperature water becomes both a stronger Lewis acid and Lewis base.

4.3.2 Oxidising species, oxygen, ozone, hydrogen peroxide and the peroxide ion

Above line (b) water may be oxidised to oxygen while at very high potentials it may also be oxidised to ozone, Equation 11'. This last reaction is unusual for redox reactions in that under acid conditions its potential rises with increasing temperature. However, it also becomes increasingly pH dependent so that the ozone domain is increased at high pH values.

The oxidation of water to the dissolved species, hydrogen peroxide and hydrogen peroxide ion, will tend to occur above lines 5', 7' and 8'. With increasing temperature their equilibrium potentials drop and become increasingly pH dependent so that water can be more readily oxidised at higher temperatures. The ionisation of hydrogen peroxide steadily increases with temperature. Thus following the Lowry and Brönsted definition 'an acid is a proton donor', hydrogen peroxide becomes a stronger acid at higher temperatures.

The sum effect of the predominating species is illustrated by Figures 6 a – g. These figures show the areas of oxidising-acidic, oxidising-alkaline, reducing-acidic and reducing-alkaline. The overall effect on raising the temperature is for a system to become more oxidising and alkaline.

4.4 Conductivity of Water along the Saturation Vapour Pressure Curve

One of the easiest methods of monitoring water purity in industrial and nuclear boilers is by using an in-line conductivity cell. However conductivity is a function of temperature, pressure, volume (density) and, except for pure water, the concentration of dissolved salts. Wilde (1967) reported on the variation of conductivity for reactor grade water (0.4 – 0.6 $\mu\,\mho\,cm^{-1}$ at 298.16°K and 1 atm.) between the temperature range 298.16 – 573.16°K. He observed a maximum in conductivity around 523.16°K. A similar result was obtained by Brewer and Hutchens (1966) who used a high purity water (0.06 – 0.12 $\mu\,\mho\,cm^{-1}$ at 298.16°K and 1 atm.). Although not stated, the method of experiment was such that the measurements were taken along the saturation vapour pressure curve. Holzapfel (1969) reviewed the effects of pressure and temperature on the conductivity and ionic dissociation of water up to 100 kbar and 273.16°K. He showed by comparison with results at higher pressures and temperatures a maximum in conductivity was to be expected between 473.16°K and 523.16°K on the saturation vapour pressure curve.

The conductivity of pure water σ_w can be expressed in terms of equivalent conductances λ_{H^+} and λ_{OH^-} and concentrations C_{H^+} and C_{OH^-} of the ions H^+ and OH^- respectively.

$$\sigma_w = \lambda_{(H^+)} \cdot C_{(H^+)} + \lambda_{(OH^-)} \cdot C_{(OH^-)} \qquad (19)$$

The concentrations are related to the ionic product K_w by

$$K_w = f_{(H^+)} \cdot f_{(OH^-)} \cdot C_{(H^+)} \cdot C_{(OH^-)} \tag{20}$$

$f_{(H^+)}$ and $f_{(OH^-)}$ are the respective activity coefficients. These are equal to 1 at infinite dilution. At 298.16° K at 1 atm. and pH 7 Holzapfel estimated them to be 0.9996 and within experimental accuracy unaffected by temperature and pressure. Hence, defining the limiting equivalent conductance Λ°_w

$$\Lambda^\circ_w = \lambda^\circ_{(H^+)} + \lambda^\circ_{(OH^-)} \tag{21}$$

where superscript ° refers to infinite dilution, we may rearrange Equation 19 to

$$\log \sigma_w = \log \Lambda^\circ_w + \frac{1}{2} \log K_w \tag{22}$$

Thus conductivity is a log function of two terms, the limiting equivalent conductance Λ°_w and the ionic product K_w. The present work gives no information about the variation of Λ°_w with temperature, although Holzapfel (1969) derived the empirical equation

$$\Lambda^\circ_w = 3.4 \times 10^{-\left[\frac{.00}{T-175}\right]} \text{ litres } \mho^{-1} \text{ cm}^{-1} \text{ mole}^{-1} \tag{23}$$

with T in degrees absolute.

However the variation of the ionic product K_w with temperature may be described exactly by Equation 1. This may be rewritten as

$$\log K_w = \frac{\Delta G_f(T,H^+) + \Delta G_f(T,OH^-) - \Delta G_f(T,H_2O)}{2.303 \; R \; T} \tag{24}$$

substituting for the values of ΔG_f, Equation 24 rearranges to

$$\log K_w = -316.6 + 12728.9T^{-1} + 127.3T^{-1} \log T - 0.105T + 4.8 \times 10^{-5} T^2 . \tag{25}$$

There have been several attempts to describe the variation of K_w with temperature. Harned and Robinson (1940) considered five possible equations from the very limited thermodynamic data then available between the temperature range 273.16 - 333.16° K. In spite of the limited range they did predict a maximum for K_w at 512.16° K. Clever (1968) listed values of K_w with temperature derived from data reported as late as 1963. There were a very limited number of values above 373.16° K but he did indicate a maximum in K_w at about 493.16° K. Briere (1968), using the model Born equation, derived

$$\log K_w(T) = \frac{16314.7 - 590024/\epsilon T}{2.303 \; R \; T} \tag{26}$$

where ϵ was the dielectric constant. This equation predicted a maximum at 453.16° K. Quist (1970) has examined the variation of K_w with temperature and density. He was able to demonstrate that the logarithm of the ionic product increased linearly with the logarithm of the molar concentration of water (at constant temperature) and also increased linearly with temperature (at constant density). He derived the following equation

$$\log K_w(T) = -33.05 - 3050 \; T^{-1} + 16.8 \log C_{H_2O} \tag{27}$$

where C_{H_2O} is the molar concentration of water.

Equation 25 is completely independent of any special model and was derived using the formal thermodynamic definitions and thermodynamic data. As such Equation 25 may be considered to be the most complete description of the variation of the ionic product with water within the framework of thermodynamics. It is, however, limited to the saturation vapour pressure curve. If the system is to exist above this curve then Quist's derived equation must be used.

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List of Symbols

Symbol	
$\bar{C}_p$	Partial molal heat capacity, cal. $mole^{-1}$ deg^{-1} Subscripted for solute Superscripted ° for a defined standard state
C	Concentration in molar units
E_o	Electromotive force of cell for a defined standard state, in volts
$\Delta\bar{G}^\circ_f$	Partial molal Gibbs energy of formation for a defined standard state Post-scripted by bracketed terms for temperature and species, cal. $mole^{-1}$
$\Delta\bar{H}^\circ_f$	Partial molal enthalpy of formation for a defined standard state Post-scripted by bracketed terms for temperature, cal. $mole^{-1}$
K_w	The ionic product of water
p	Pressure in atmospheres
pH	Hydrogen ion concentration
$\bar{S}$	Partial molal entropy in e.u.
rH	Hydrogen gas concentration
rO	Oxygen gas concentration
ϵ	Dielectric constant
λ	Equivalent conductance Subscripted for species Superscripted ° for infinite dilution
Λ°_w	Limiting equivalent conductance of water
σ_w	Conductivity of water $\mho\,cm^{-1}$

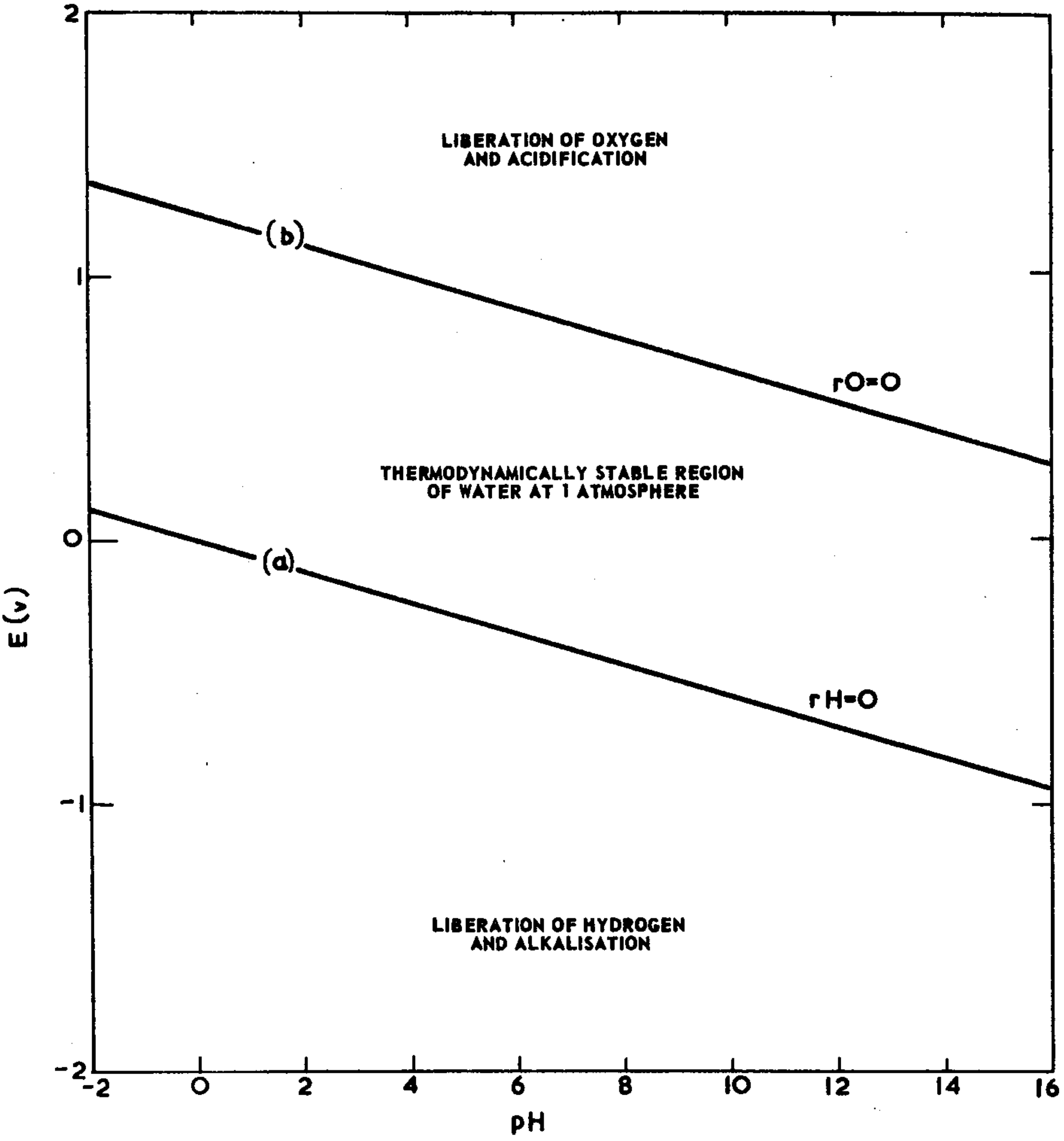

FIGURE 1a. DOMAIN OF THERMODYNAMIC STABILITY OF WATER UNDER 1 ATMOSPHERE OF H_2 OR O_2 AT 298.16°K

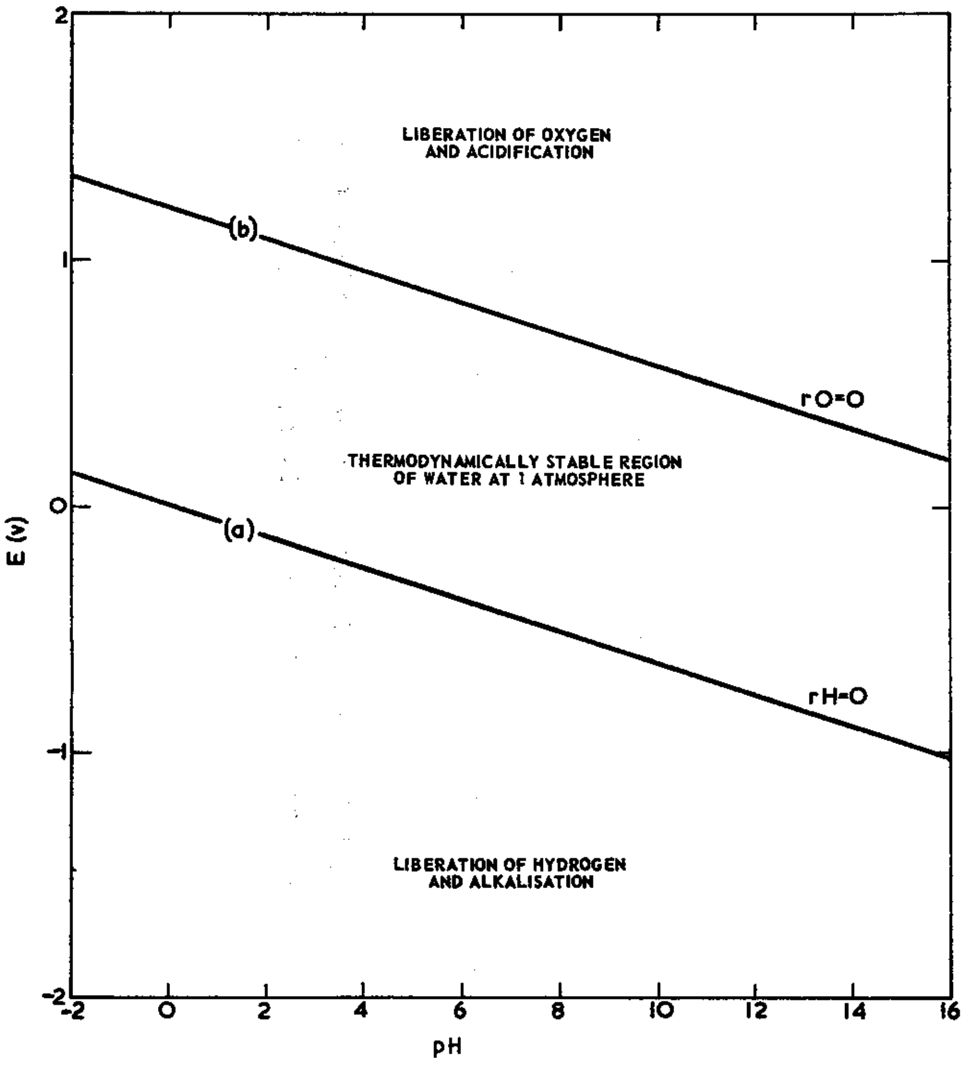

FIGURE 1b. DOMAIN OF THERMODYNAMIC STABILITY OF WATER UNDER 1 ATMOSPHERE OF H_2 OR O_2 AT 323.16°K

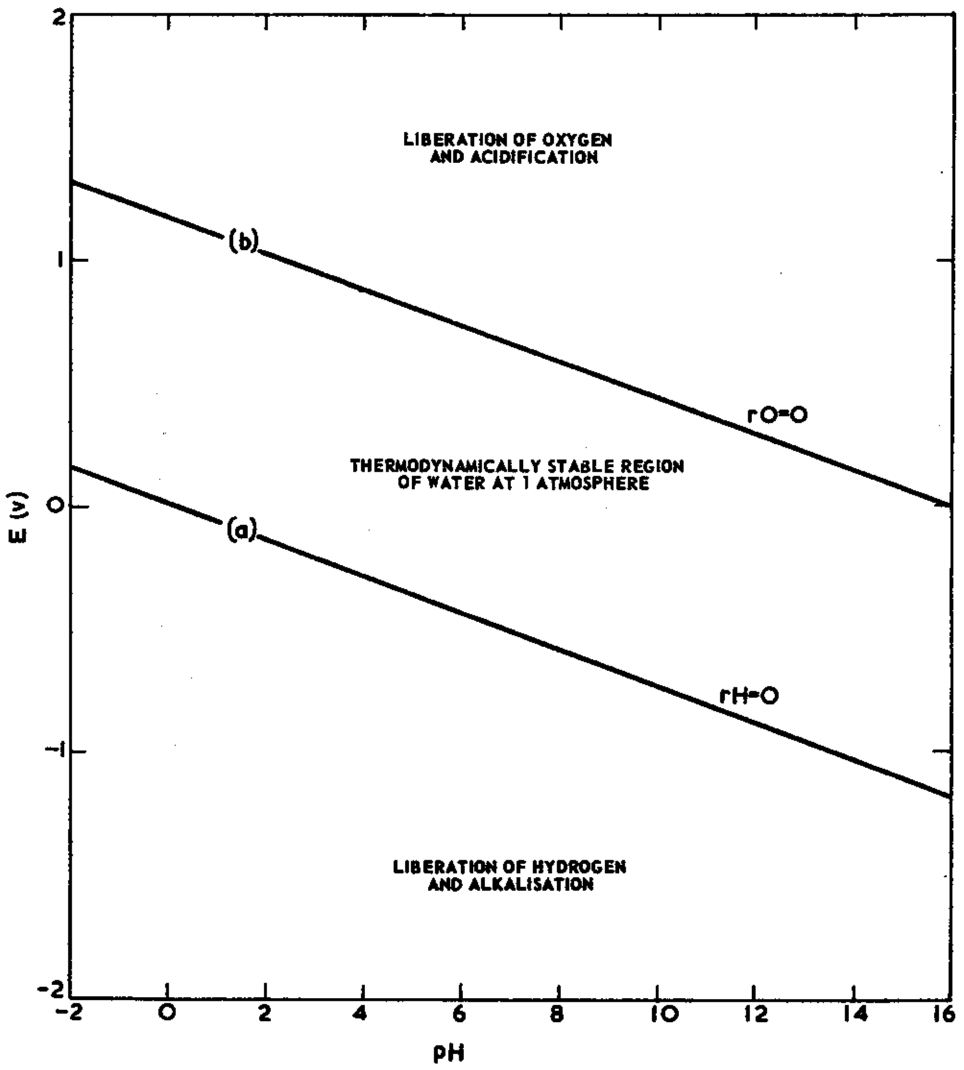

FIGURE 1c. DOMAIN OF THERMODYNAMIC STABILITY OF WATER UNDER 1 ATMOSPHERE OF H_2 OR O_2 AT 373.16°K

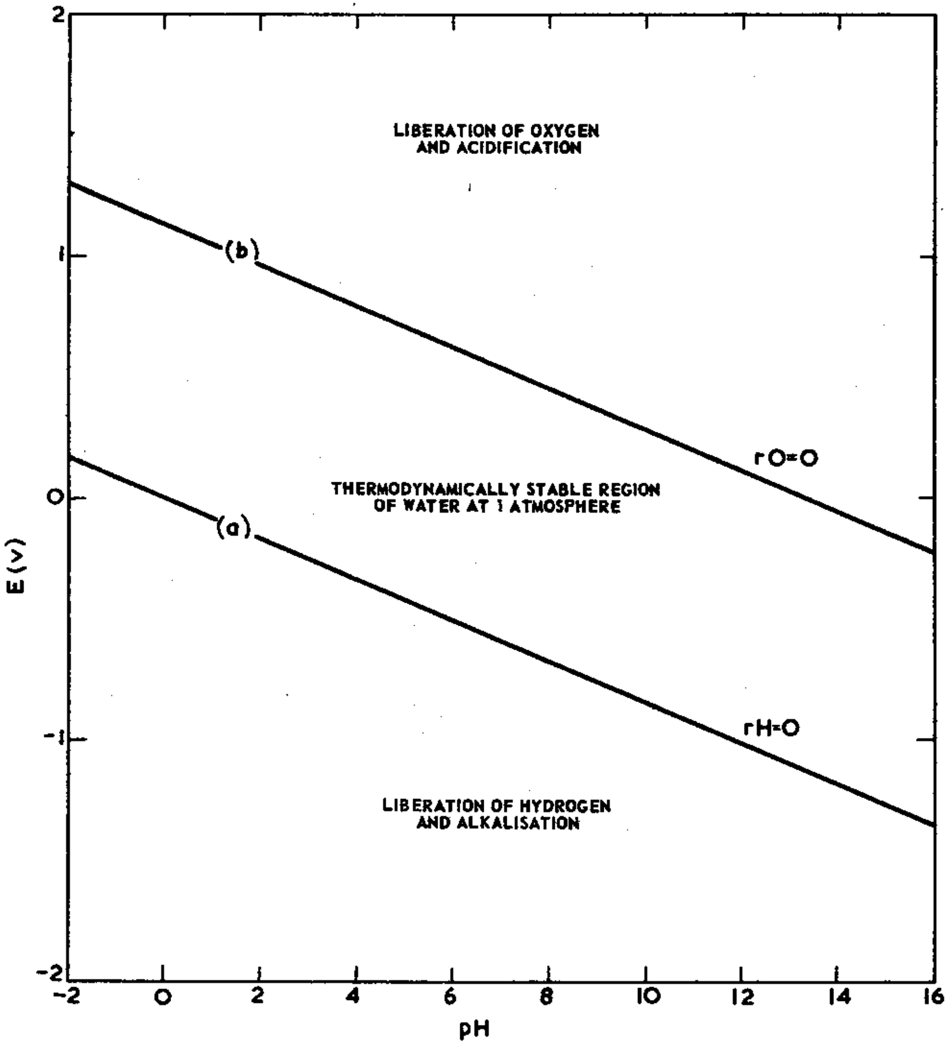

FIGURE 1d. DOMAIN OF THERMODYNAMIC STABILITY OF WATER UNDER 1 ATMOSPHERE OF H_2 OR O_2 AT 423.16°K

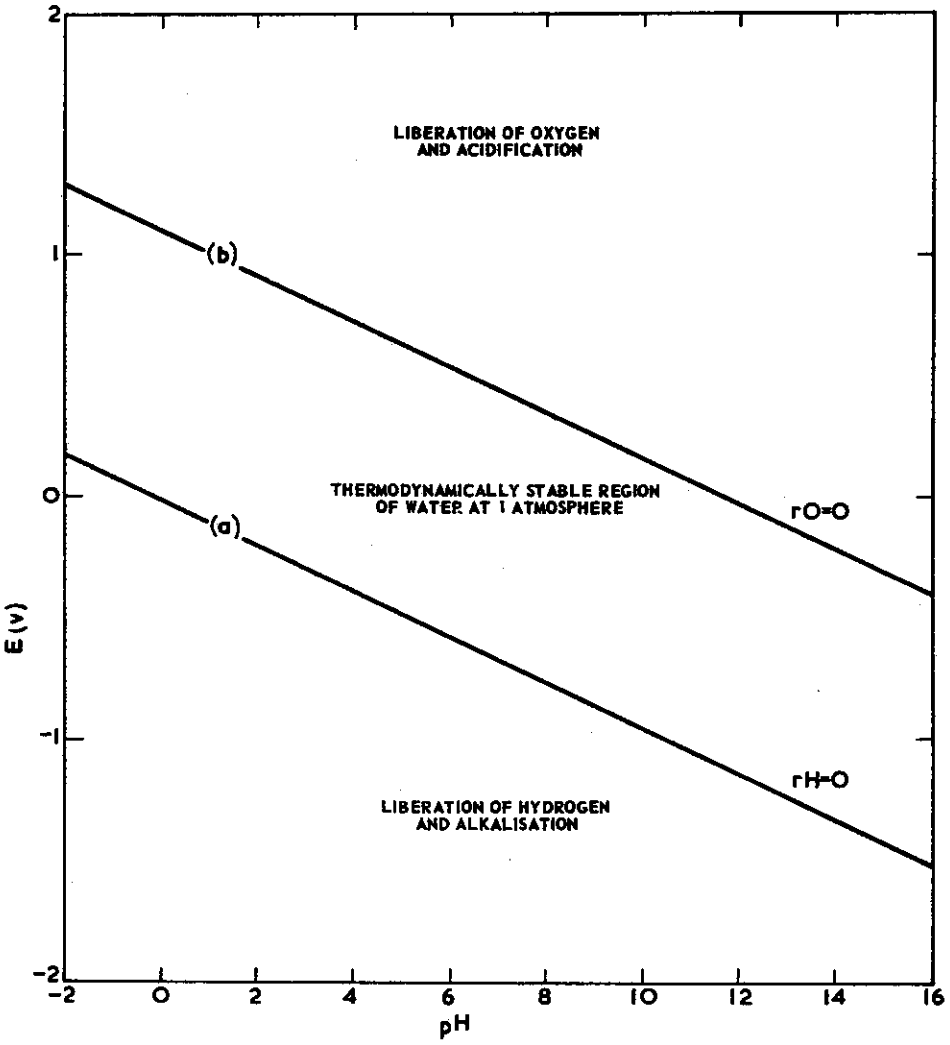

FIGURE 1e. DOMAIN OF THERMODYNAMIC STABILITY OF WATER UNDER 1 ATMOSPHERE OF H_2 OR O_2 AT 473.16°K

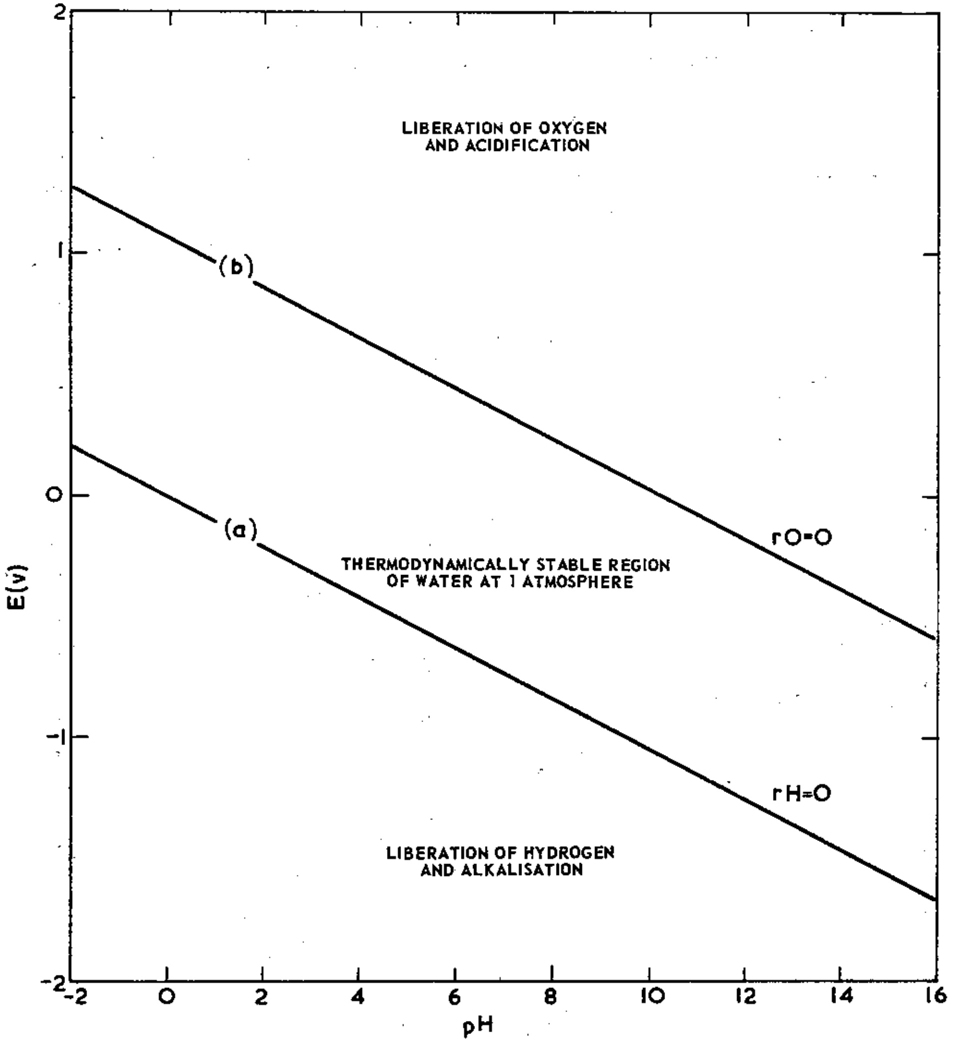

FIGURE 1f. DOMAIN OF THERMODYNAMIC STABILITY OF WATER UNDER 1 ATMOSPHERE OF H_2 OR O_2 AT 523.16°K

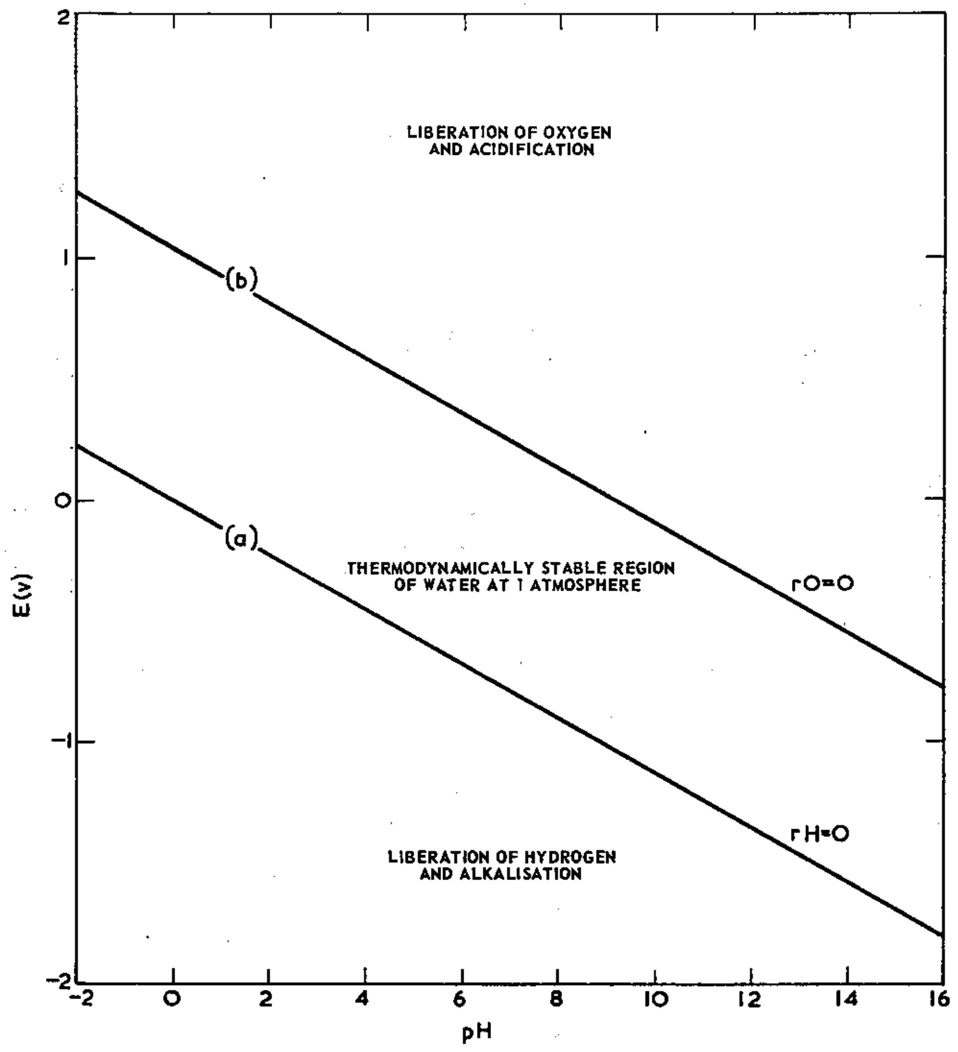

FIGURE 1g. DOMAIN OF THERMODYNAMIC STABILITY OF WATER UNDER 1 ATMOSPHERE OF H_2 OR O_2 AT 573.16°K

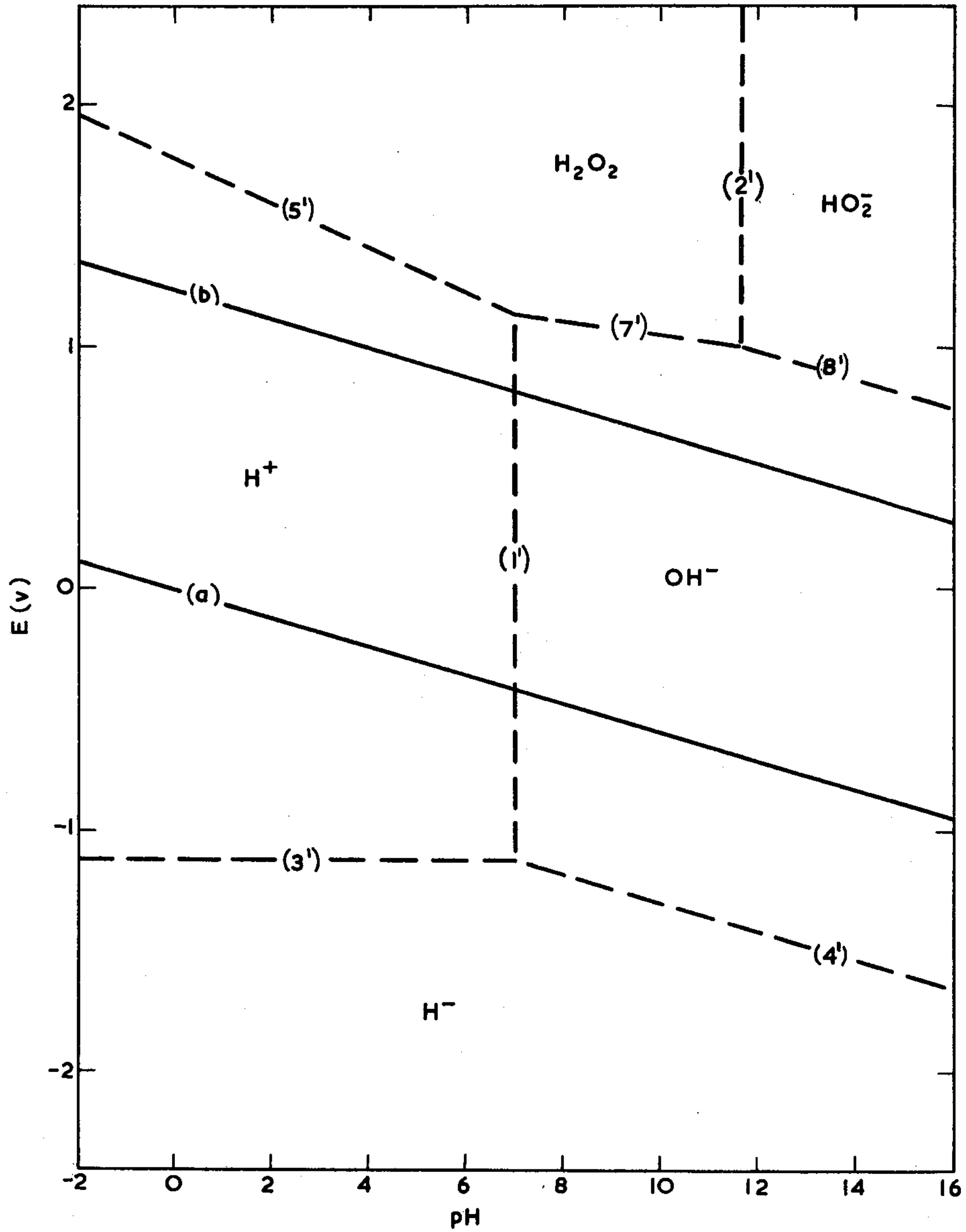

FIGURE 2a. DOMAINS OF RELATIVE PREDOMINANCE OF THE DISSOLVED SPECIES H^-, H^+, OH^-, H_2O_2 AND HO_2^- AT 298.16°K

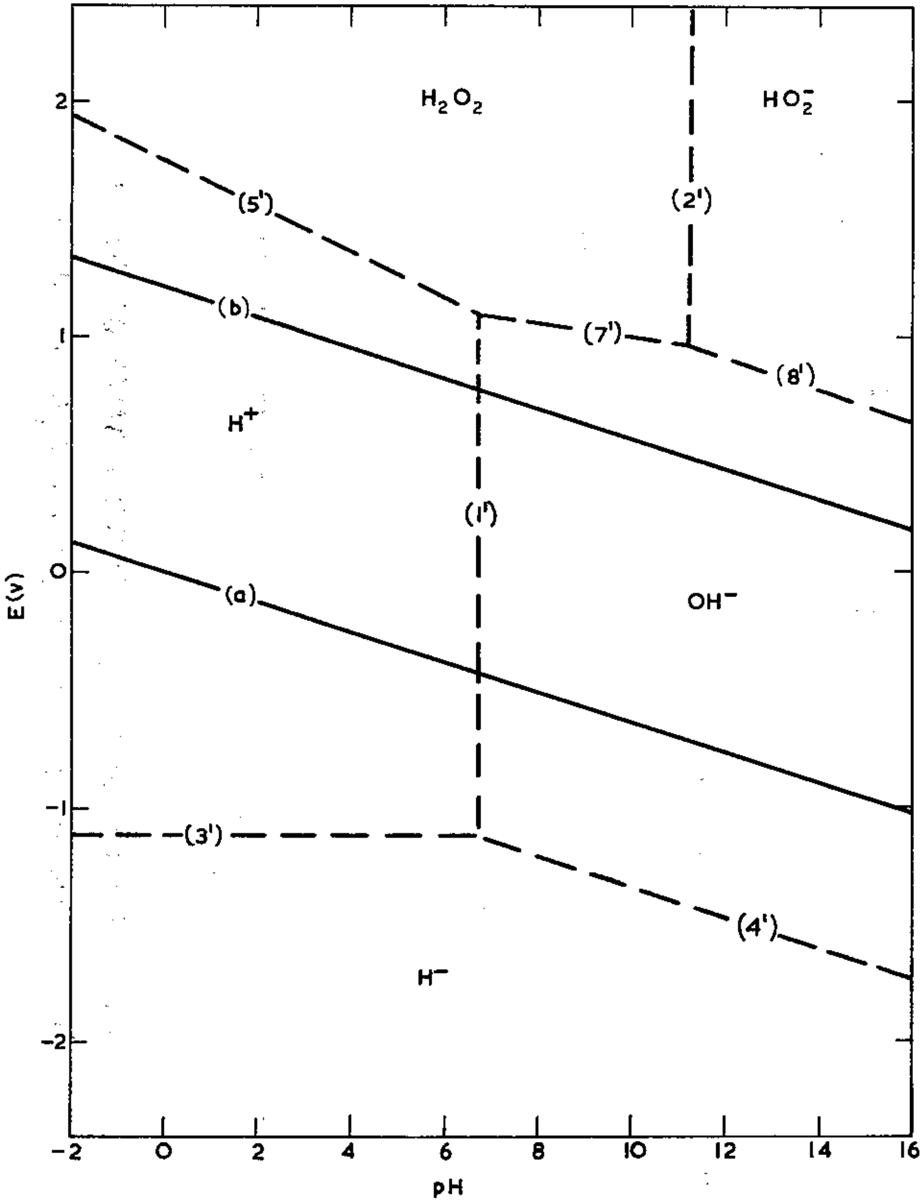

FIGURE 2b. DOMAINS OF RELATIVE PREDOMINANCE OF THE DISSOLVED SPECIES H^-, H^+, OH^-, H_2O_2 AND HO_2^- AT 323.16°K

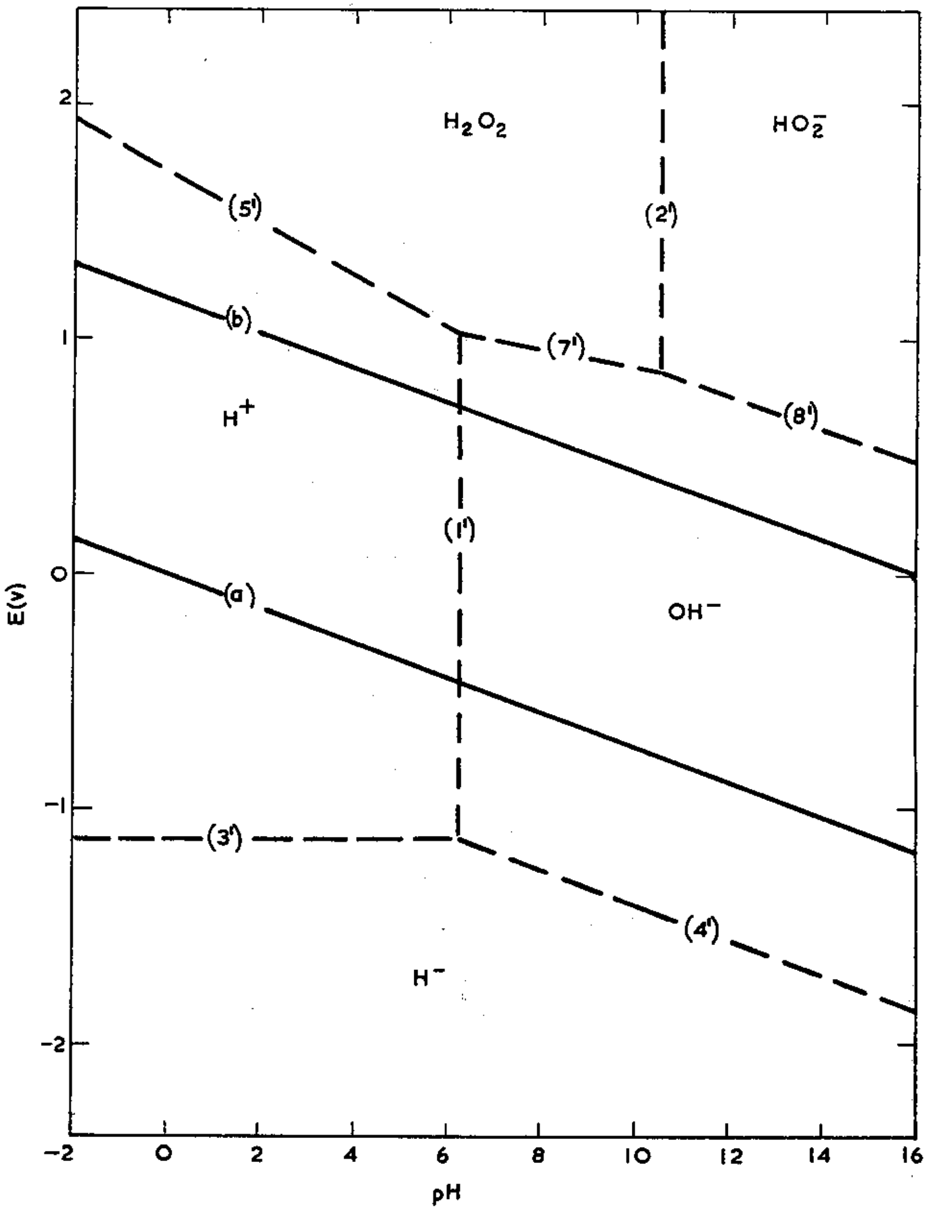

FIGURE 2c. DOMAINS OF RELATIVE PREDOMINANCE OF THE DISSOLVED SPECIES H^-, H^+, OH^-, H_2O_2 AND HO_2^- AT 373.16°K

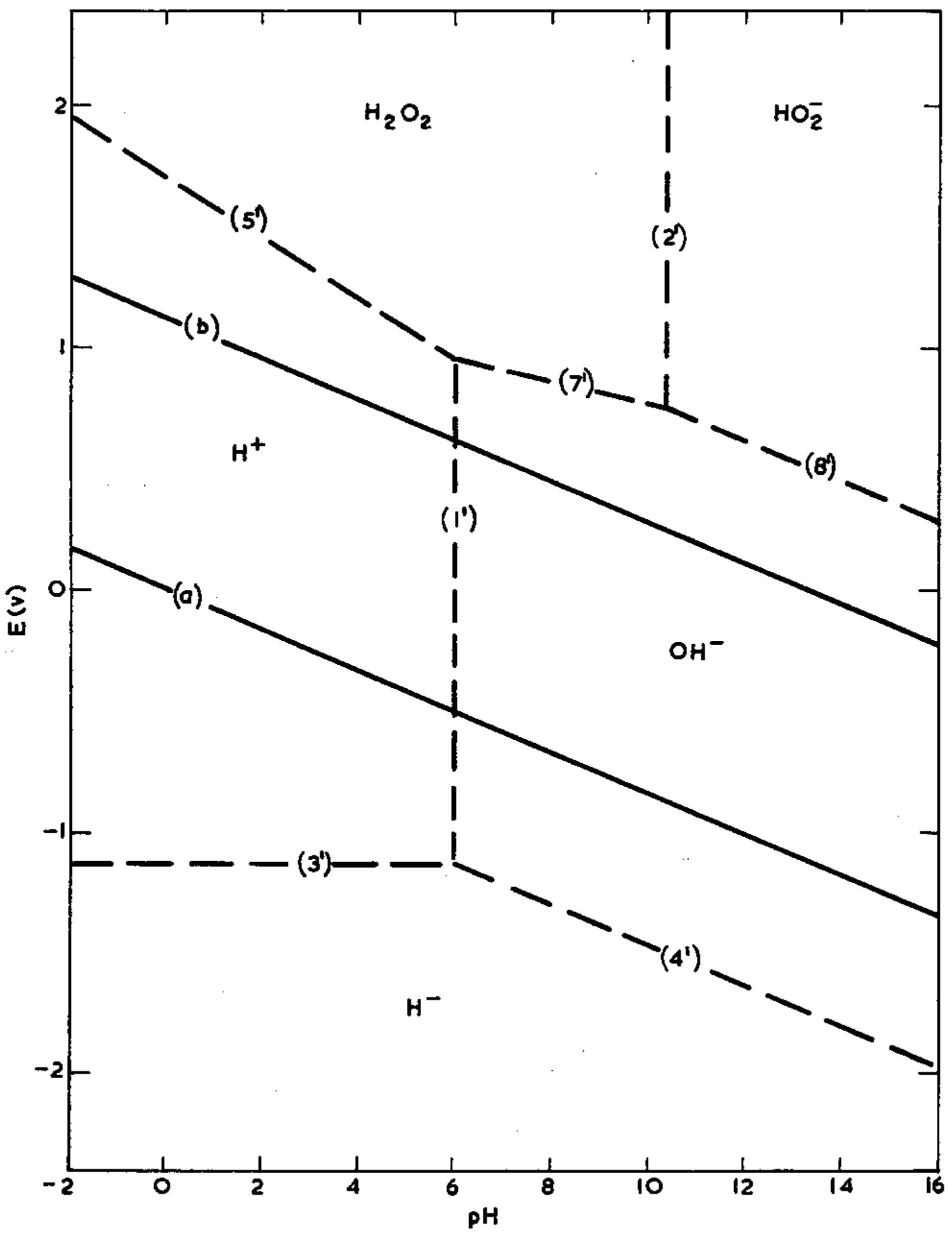

FIGURE 2d. DOMAINS OF RELATIVE PREDOMINANCE OF THE DISSOLVED SPECIES H^-, H^+, OH^-, H_2O_2 AND HO_2^- AT 423.16°K

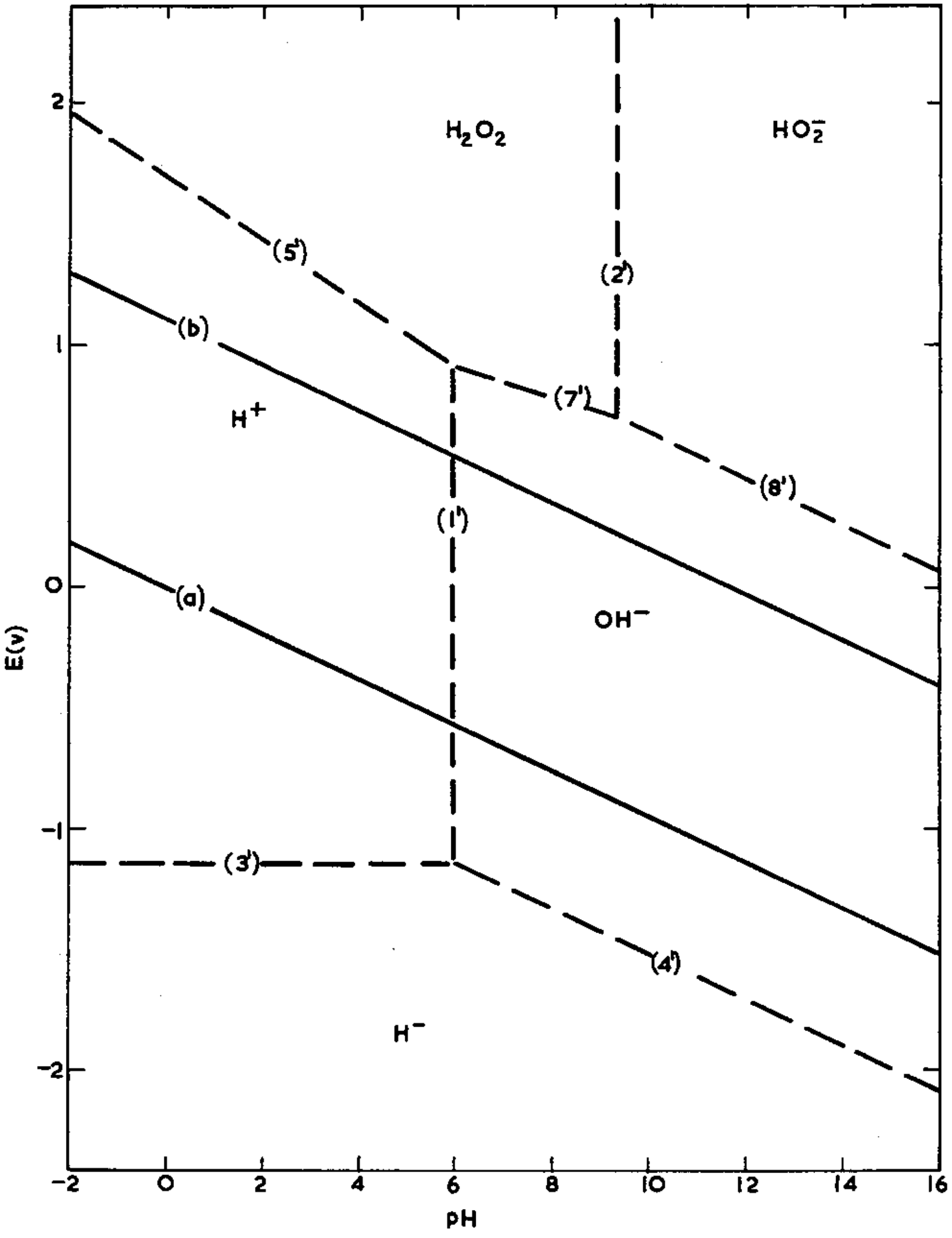

FIGURE 2e. DOMAINS OF RELATIVE PREDOMINANCE OF THE DISSOLVED SPECIES H^-, H^+, OH^-, H_2O_2 AND HO_2^-AT 473.16°K

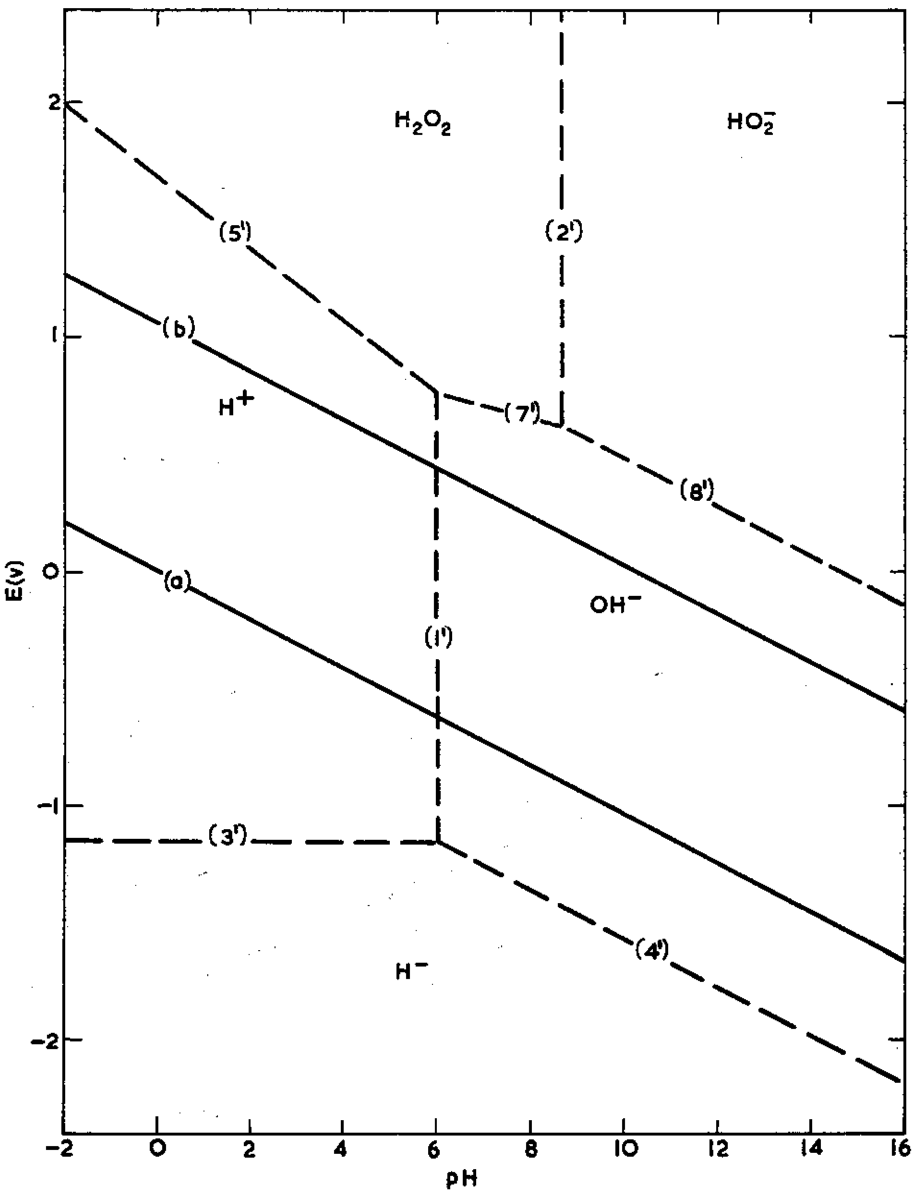

FIGURE 2f. DOMAINS OF RELATIVE PREDOMINANCE OF THE DISSOLVED SPECIES H^-, H^+, OH^-, H_2O_2 AND HO_2^- AT 523.16°K

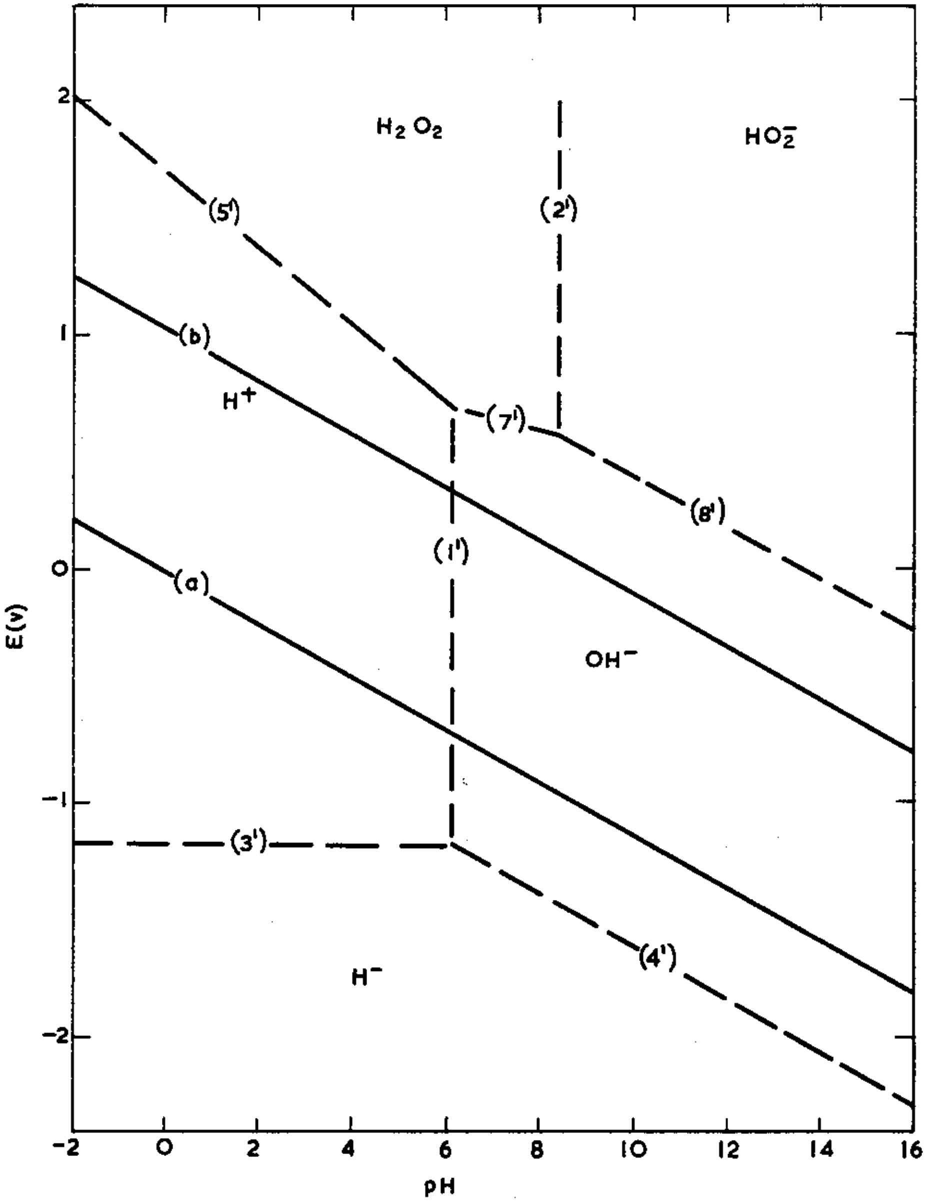

FIGURE 2g. DOMAINS OF RELATIVE PREDOMINANCE OF THE DISSOLVED SPECIES H^-, H^+, OH^-, H_2O_2 AND HO_2^- AT 573.16°K

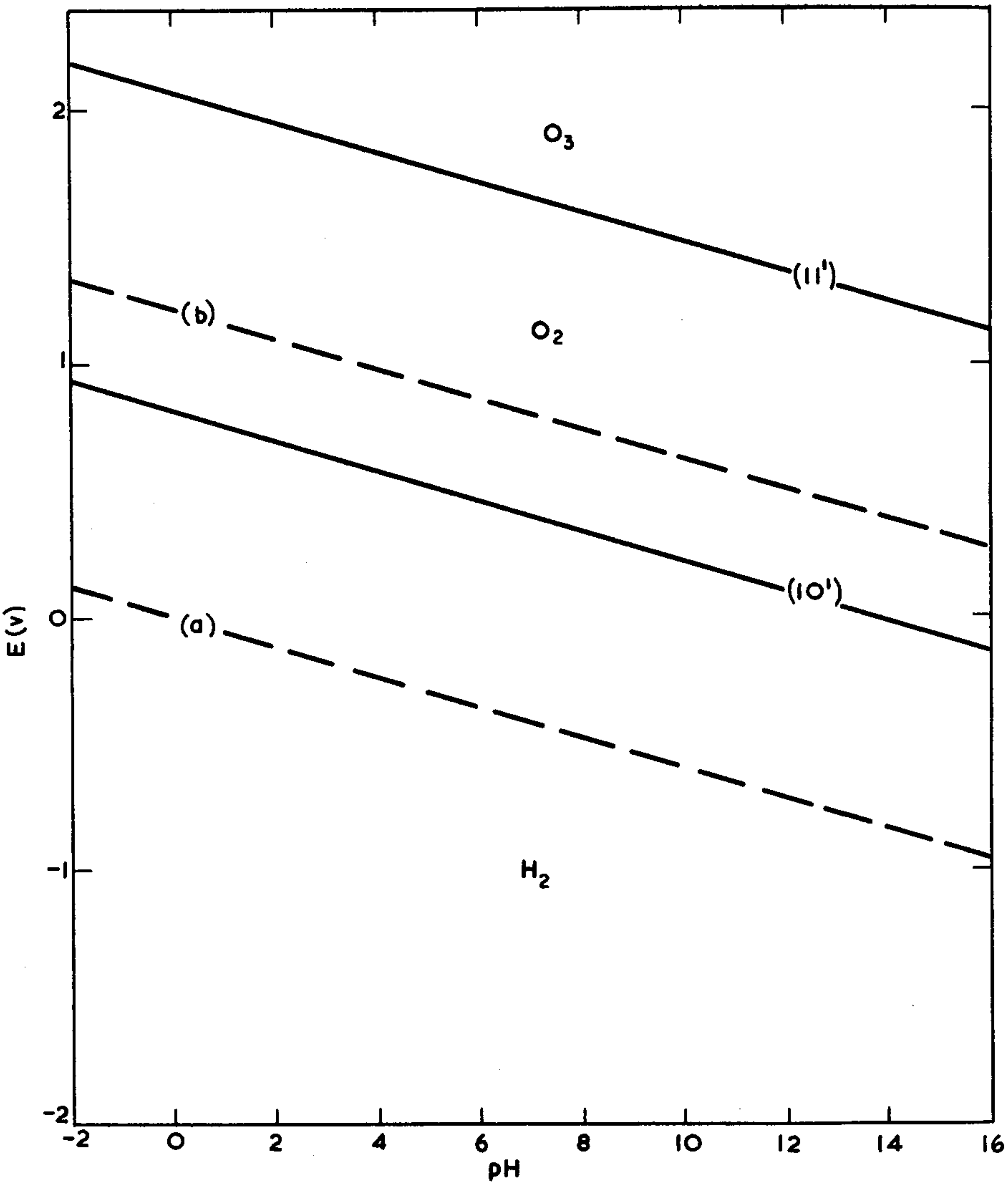

FIGURE 3a. DOMAINS OF RELATIVE PREDOMINANCE OF THE GASEOUS SUBSTANCES H_2, O_2 AND O AT 298.16°K

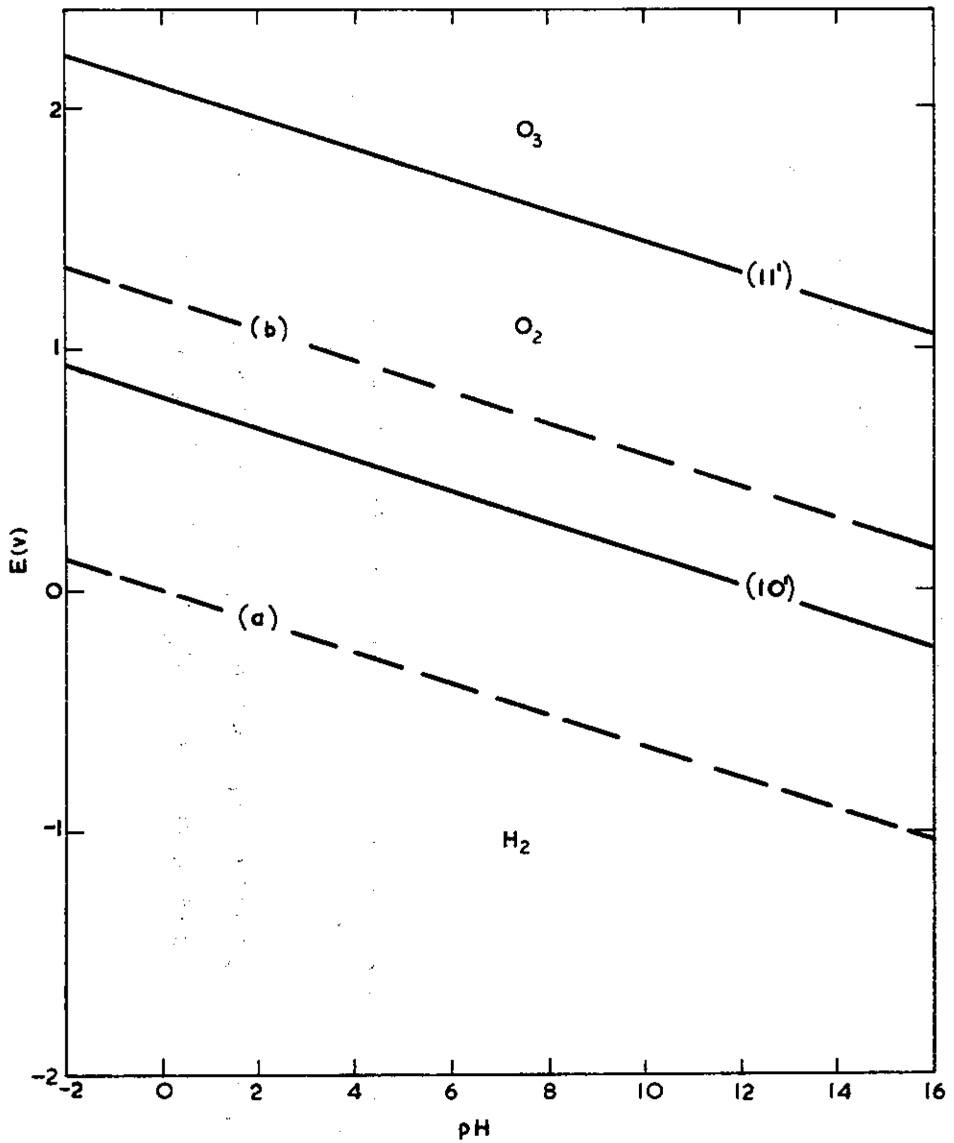

FIGURE 3b. DOMAINS OF RELATIVE PREDOMINANCE OF THE GASEOUS SUBSTANCES H_2, O_2 AND O_3 AT 323 .16°K

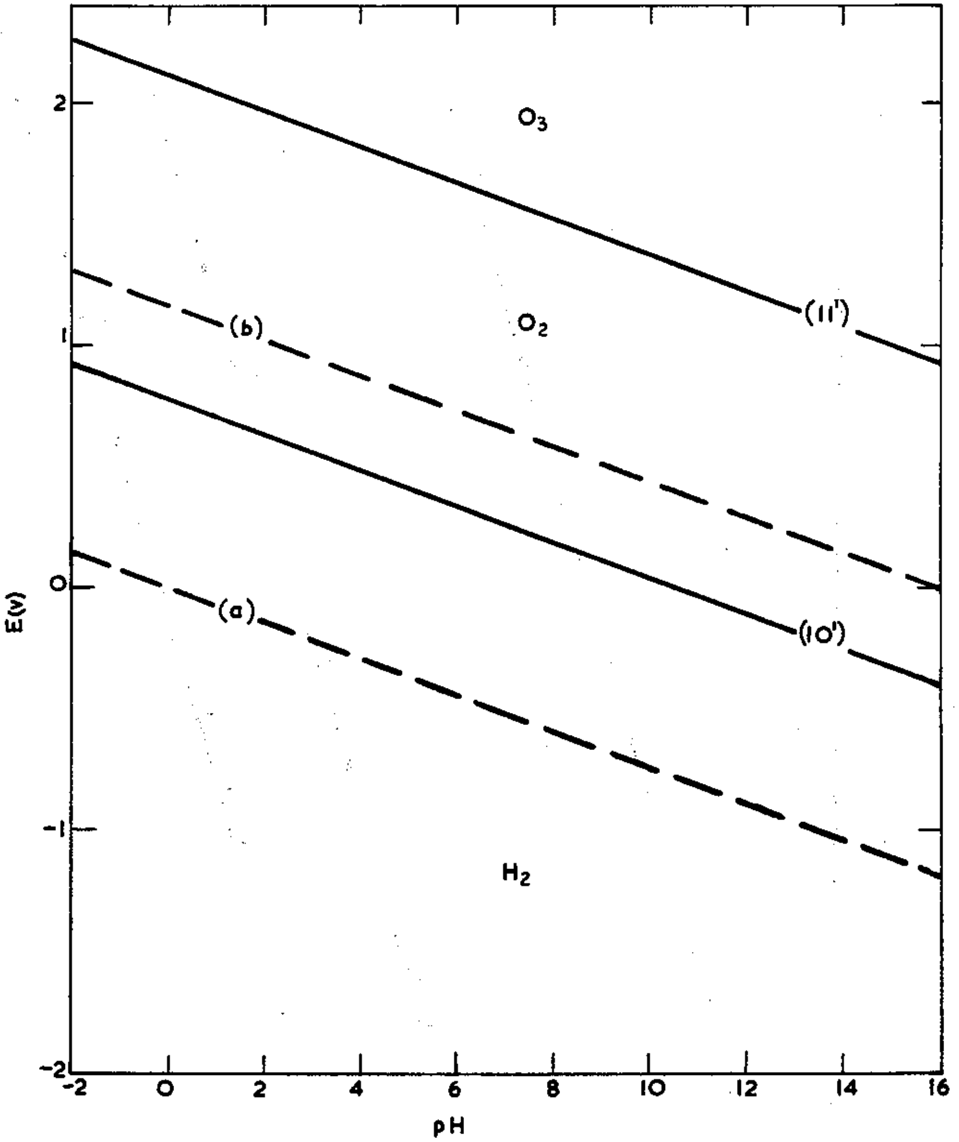

FIGURE 3c. DOMAINS OF RELATIVE PREDOMINANCE OF THE GASEOUS SUBSTANCES H_2, O_2 AND O_3 AT 373.16°K

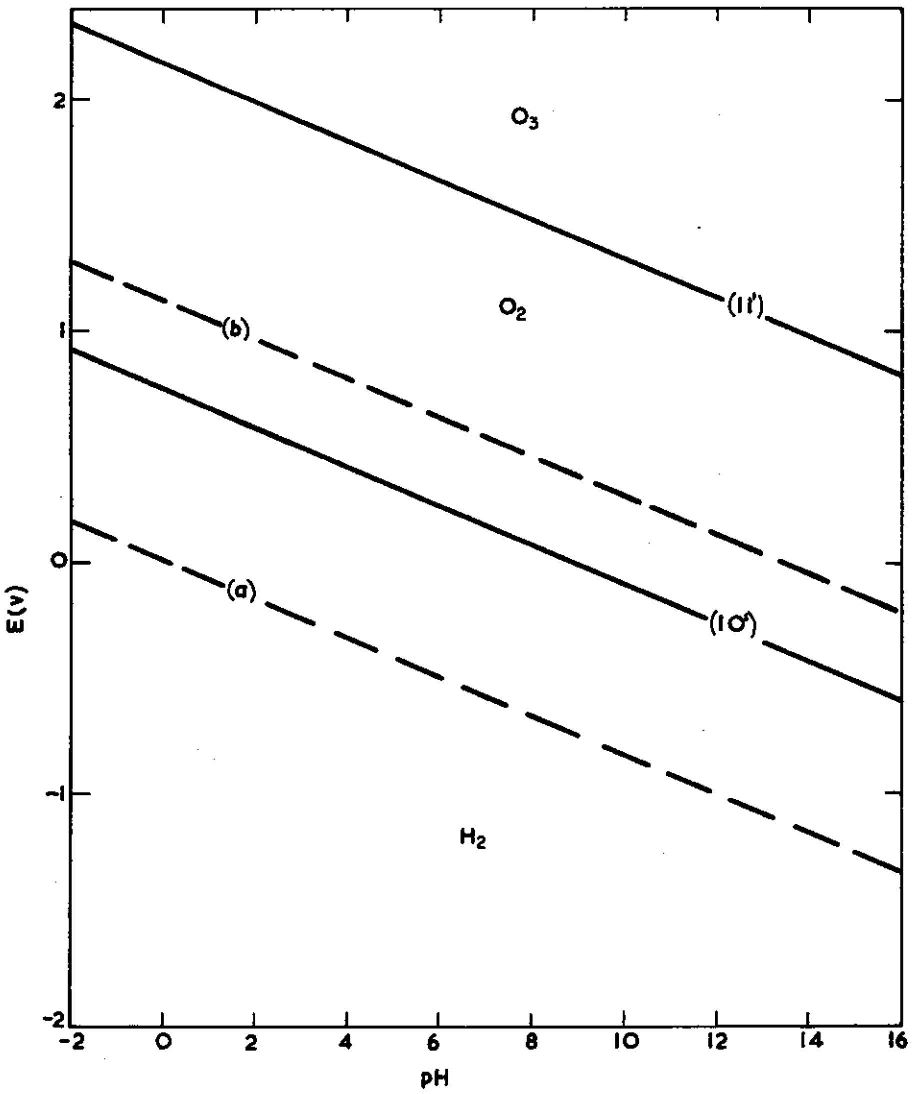

FIGURE 3d. DOMAINS OF RELATIVE DEPENDENCE OF THE GASEOUS SUBSTANCES H_2, O_2 AND O_3 AT 423.16°K

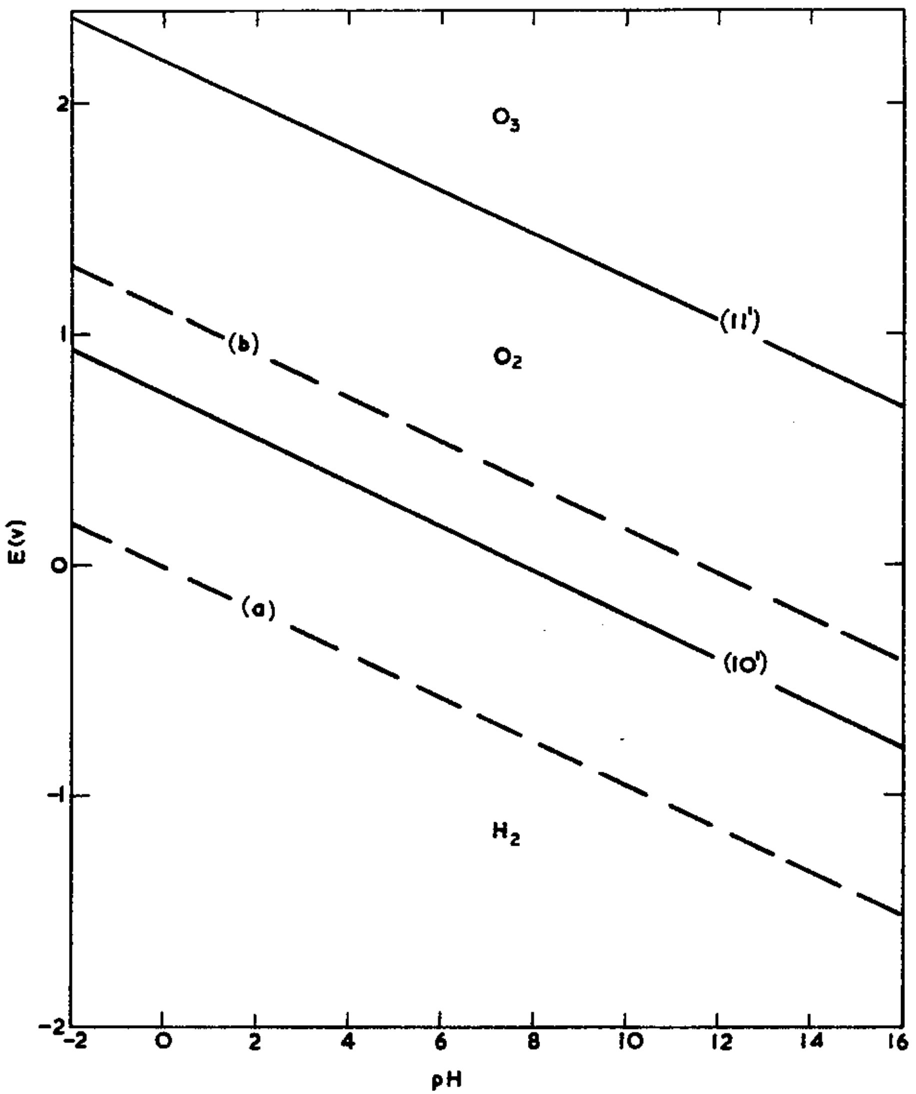

FIGURE 3e. DOMAINS OF RELATIVE PREDOMINANCE OF THE GASEOUS SUBSTANCES H_2, O_2 AND O_3 AT 473.16°K

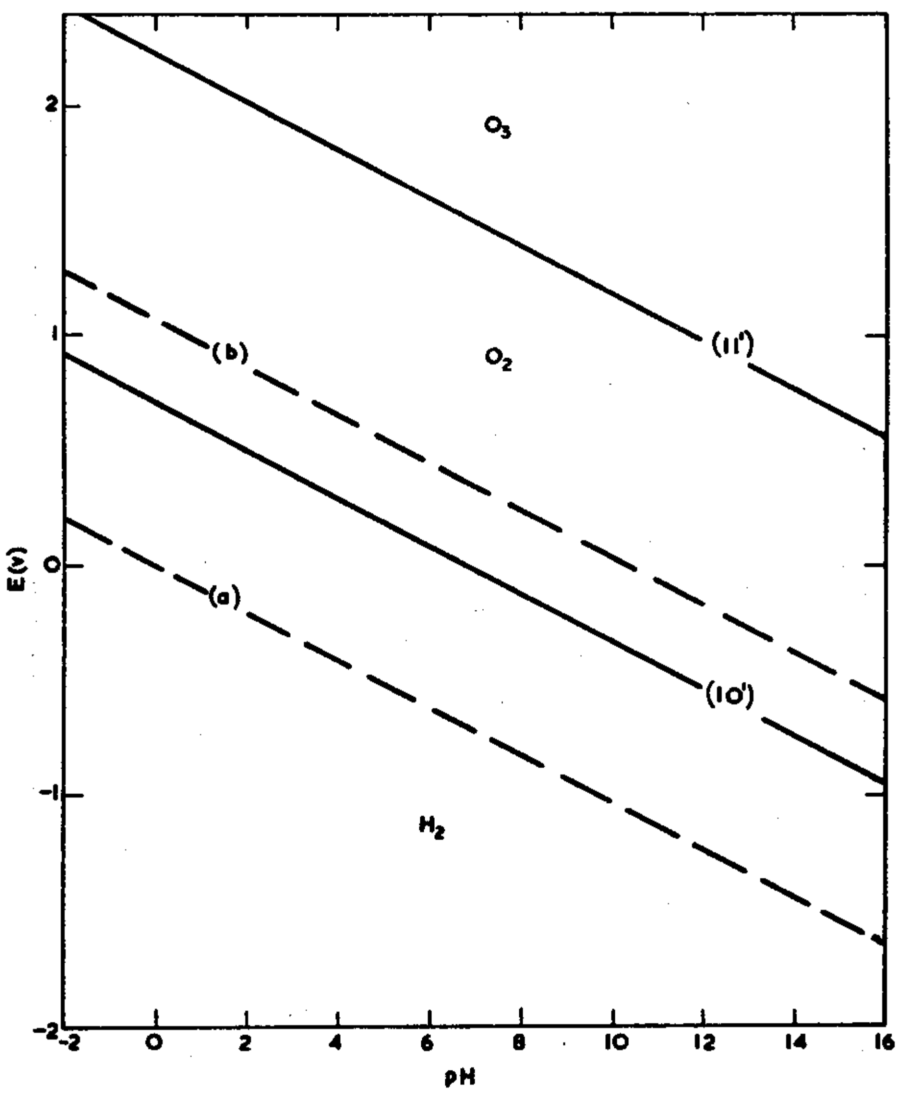

FIGURE 3f. DOMAINS OF RELATIVE PREDOMINANCE OF THE GASEOUS SUBSTANCES H_2, O_2 AND O_3 AT 523.16°K

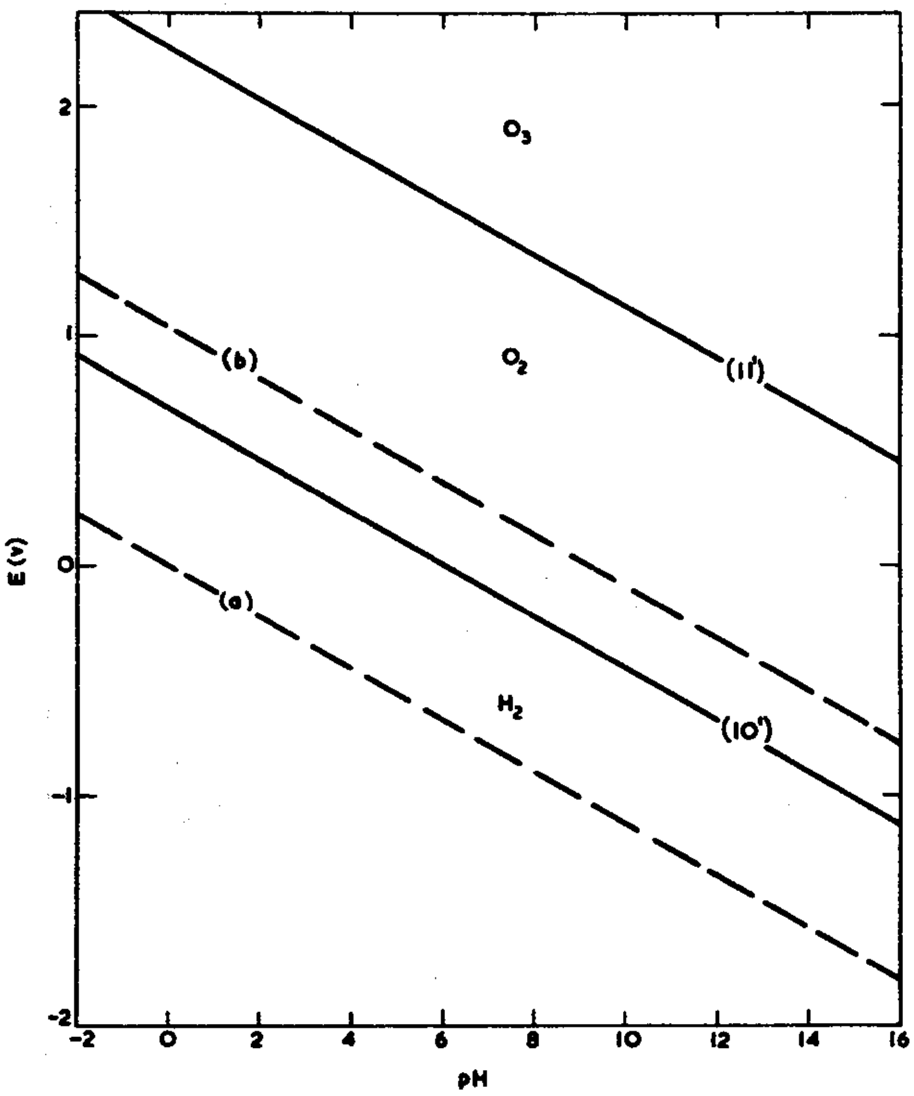

FIGURE 3g. DOMAINS OF RELATIVE PREDOMINANCE OF THE GASEOUS SUBSTANCES H_2, O_2 AND O_3 AT 573.16°K

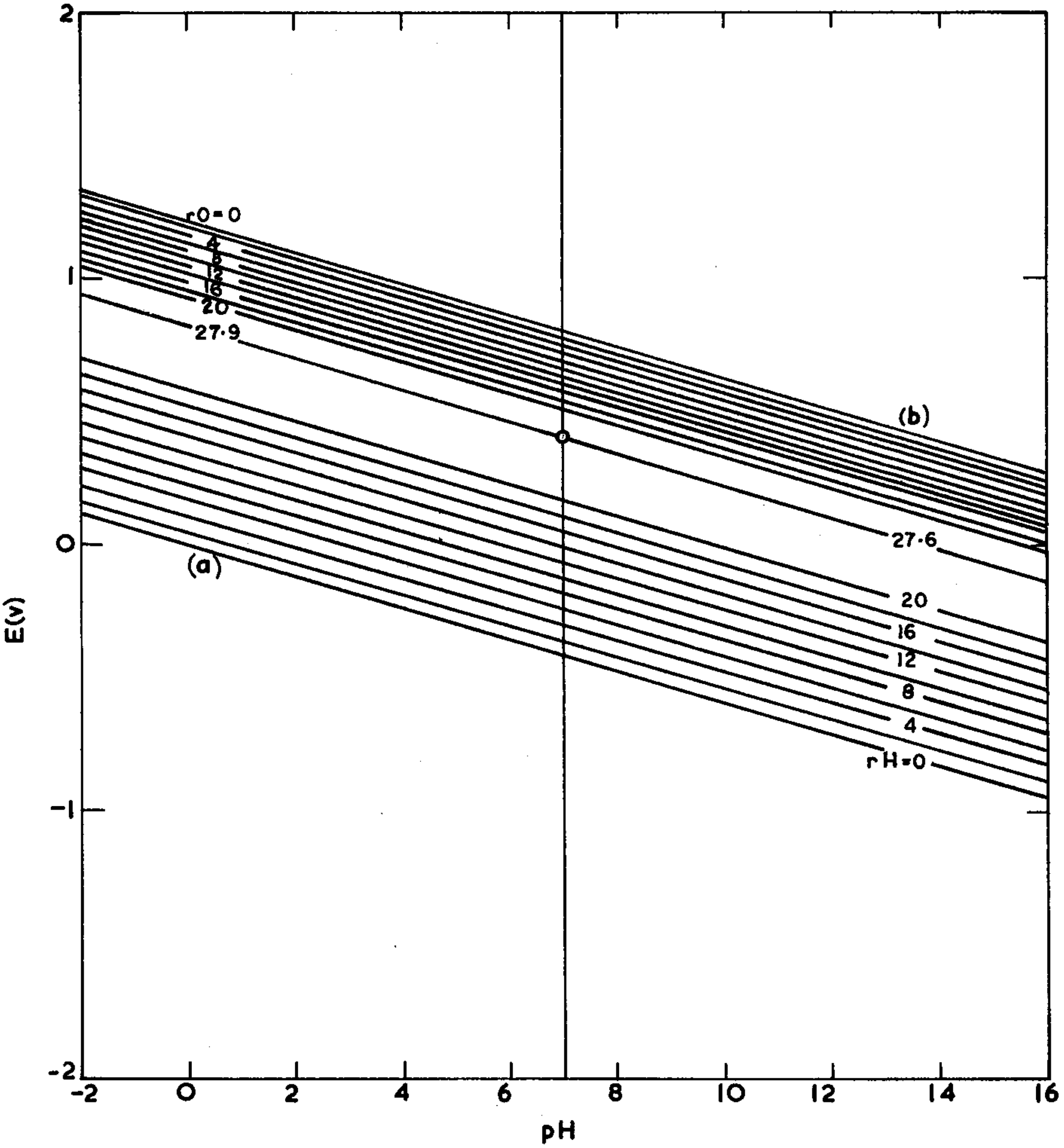

FIGURE 4a. rH AND rO OF AQUEOUS SOLUTIONS AT 298.16°K

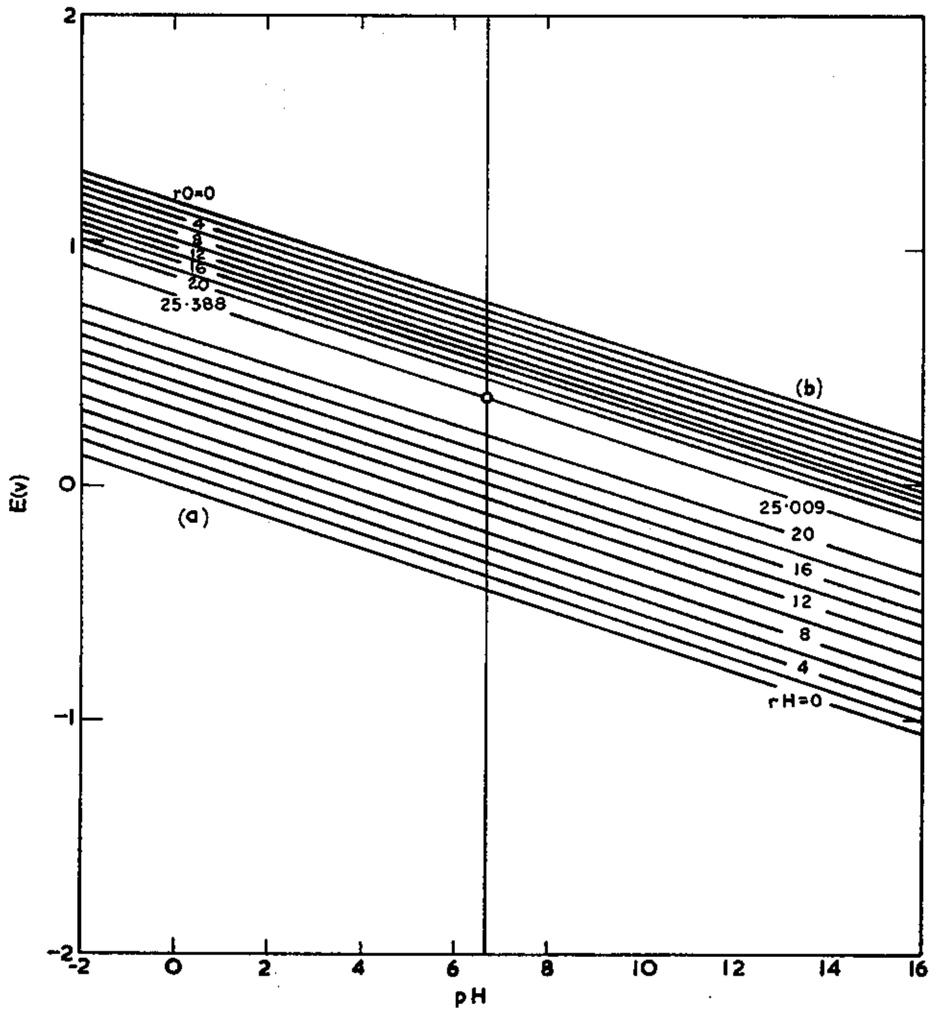

FIGURE 4b. rH AND rO OF AQUEOUS SOLUTIONS AT 323.16°K

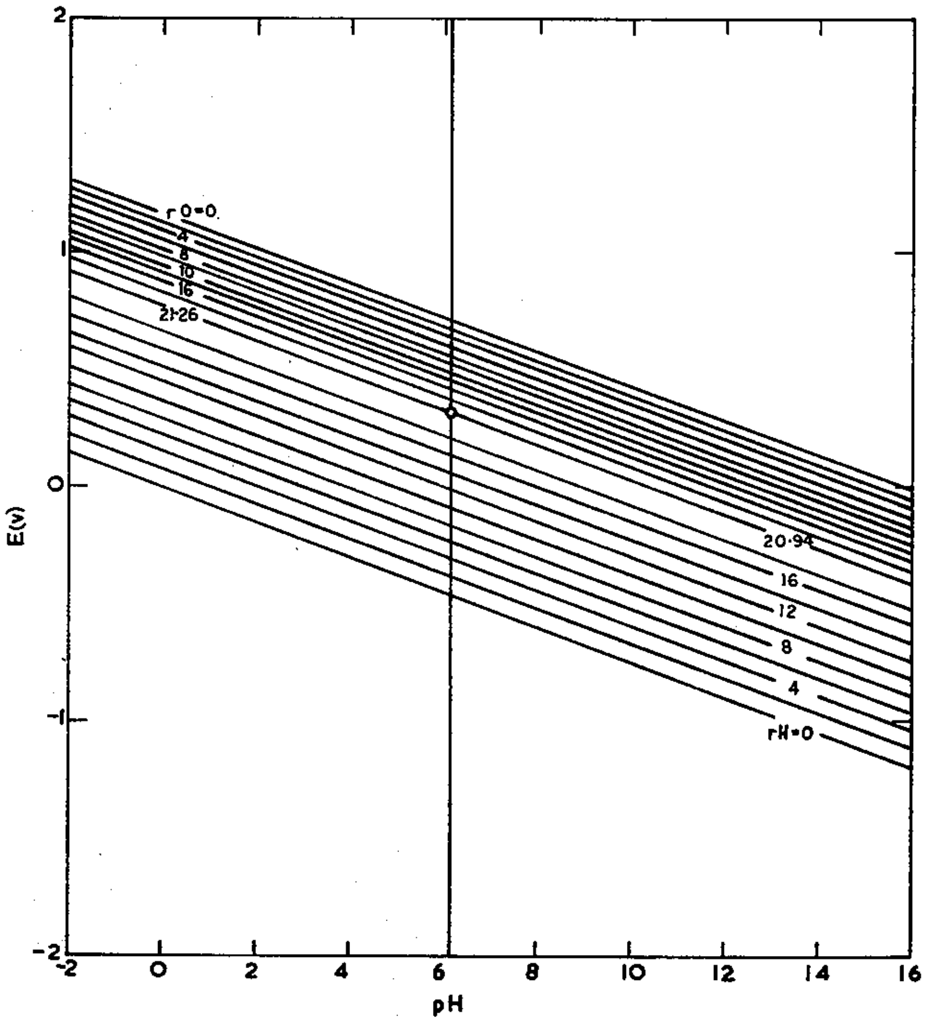

FIGURE 4c. rH AND rO OF AQUEOUS SOLUTIONS AT 373.16°K

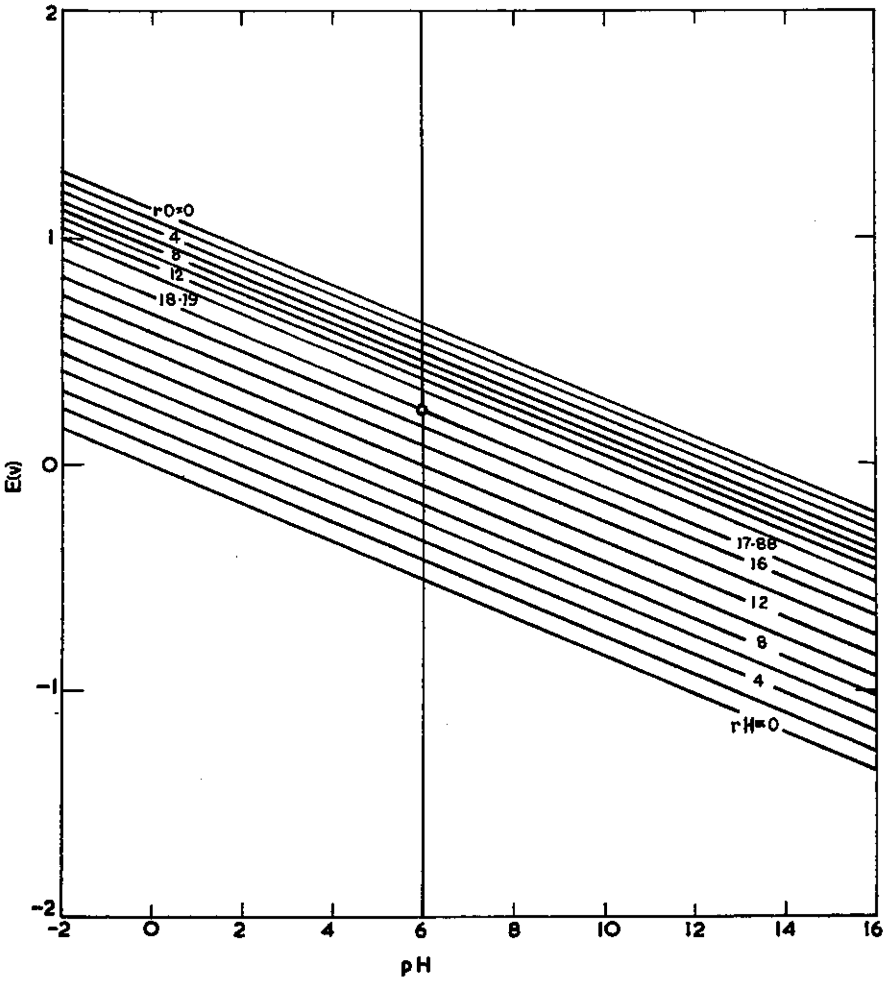

FIGURE 4d. rH AND rO OF AQUEOUS SOLUTIONS AT 423.16°K

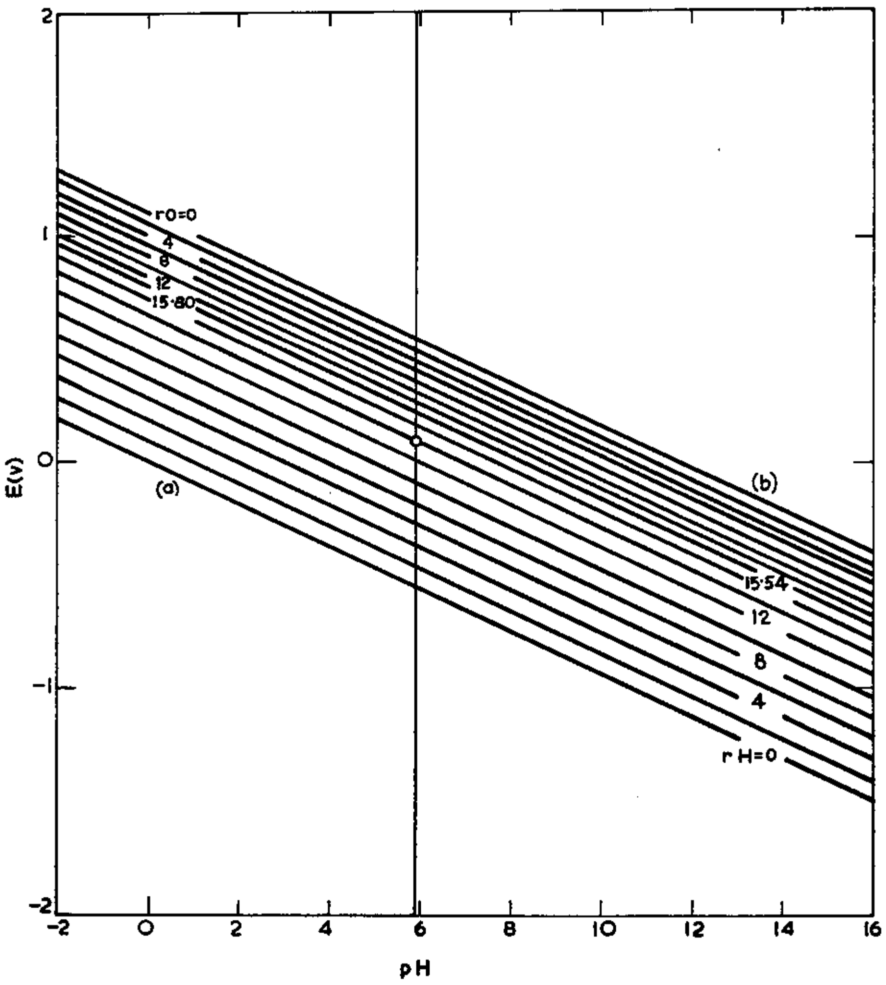

FIGURE 4e. rH AND rO OF AQUEOUS SOLUTIONS AT 473.16°K

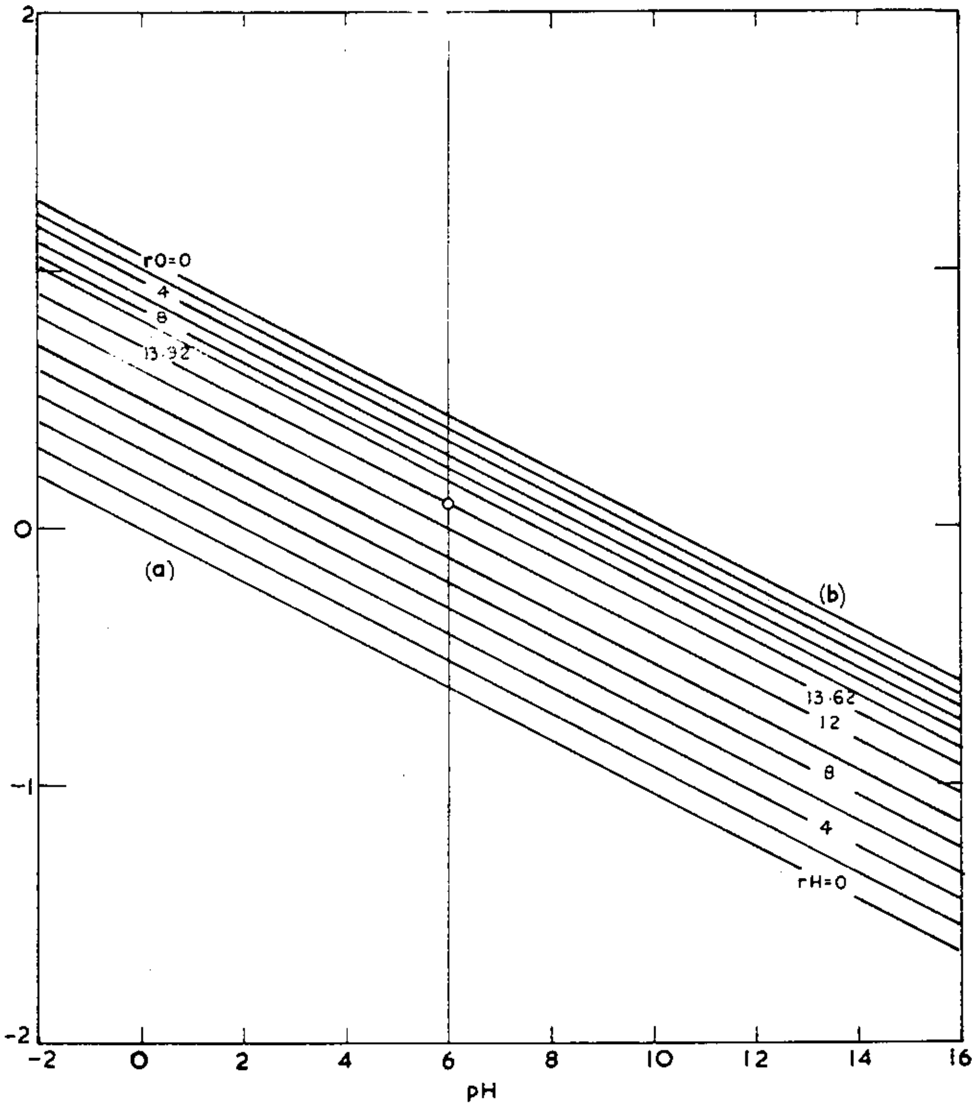

FIGURE 4f. rH AND rO OF AQUEOUS SOLUTIONS AT 523.16 °K

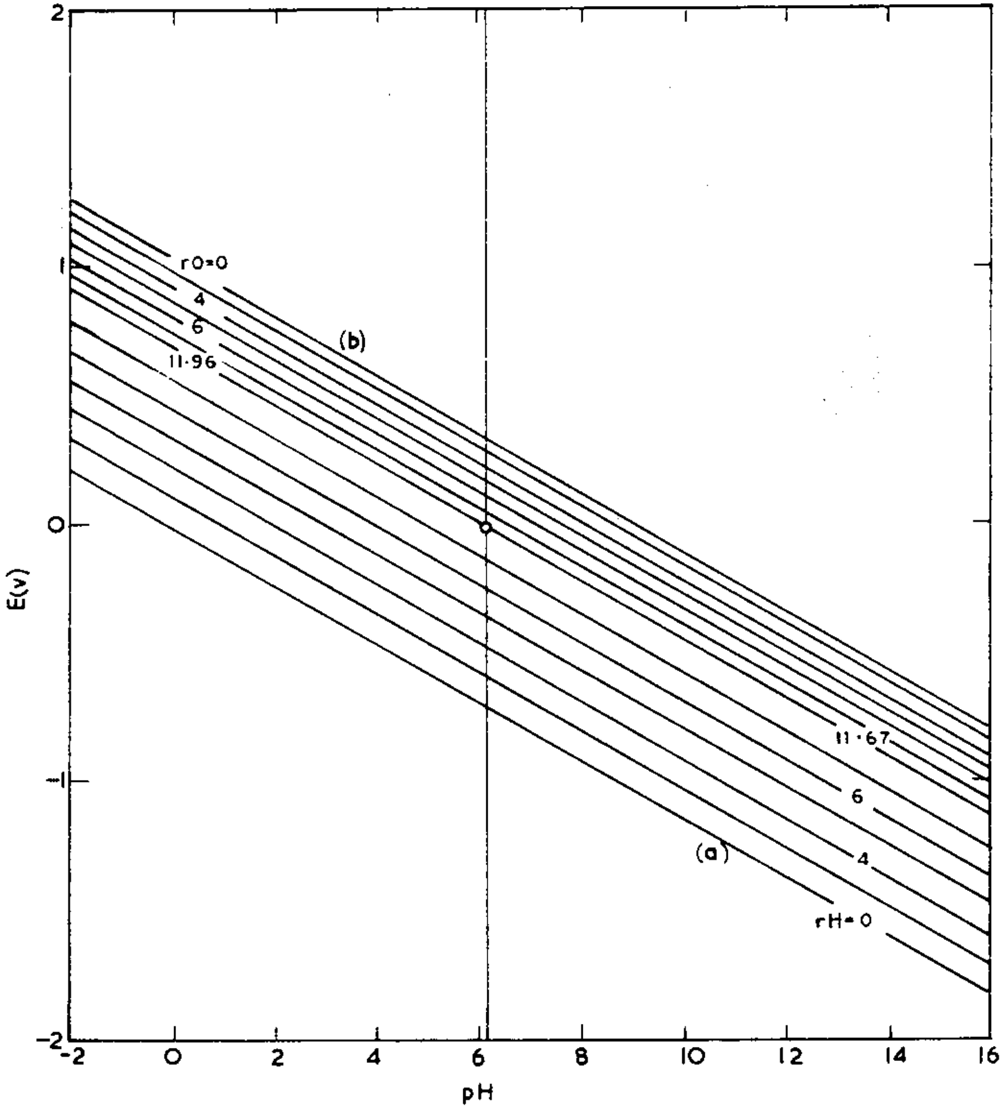

FIGURE 4g. rH AND rO OF AQUEOUS SOLUTIONS AT 573.16 °K

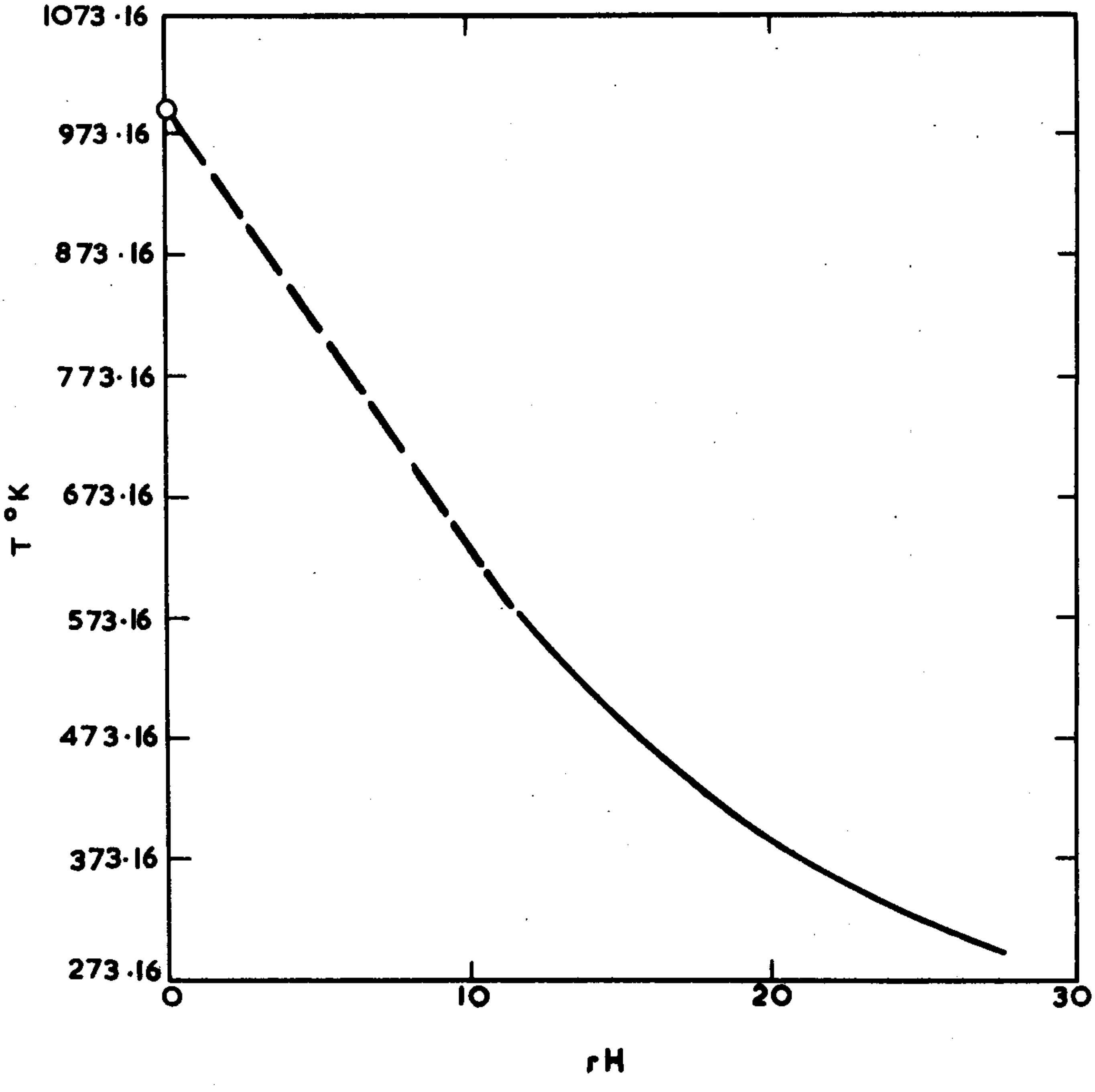

FIGURE 5. rH VERSUS TEMPERATURE °K

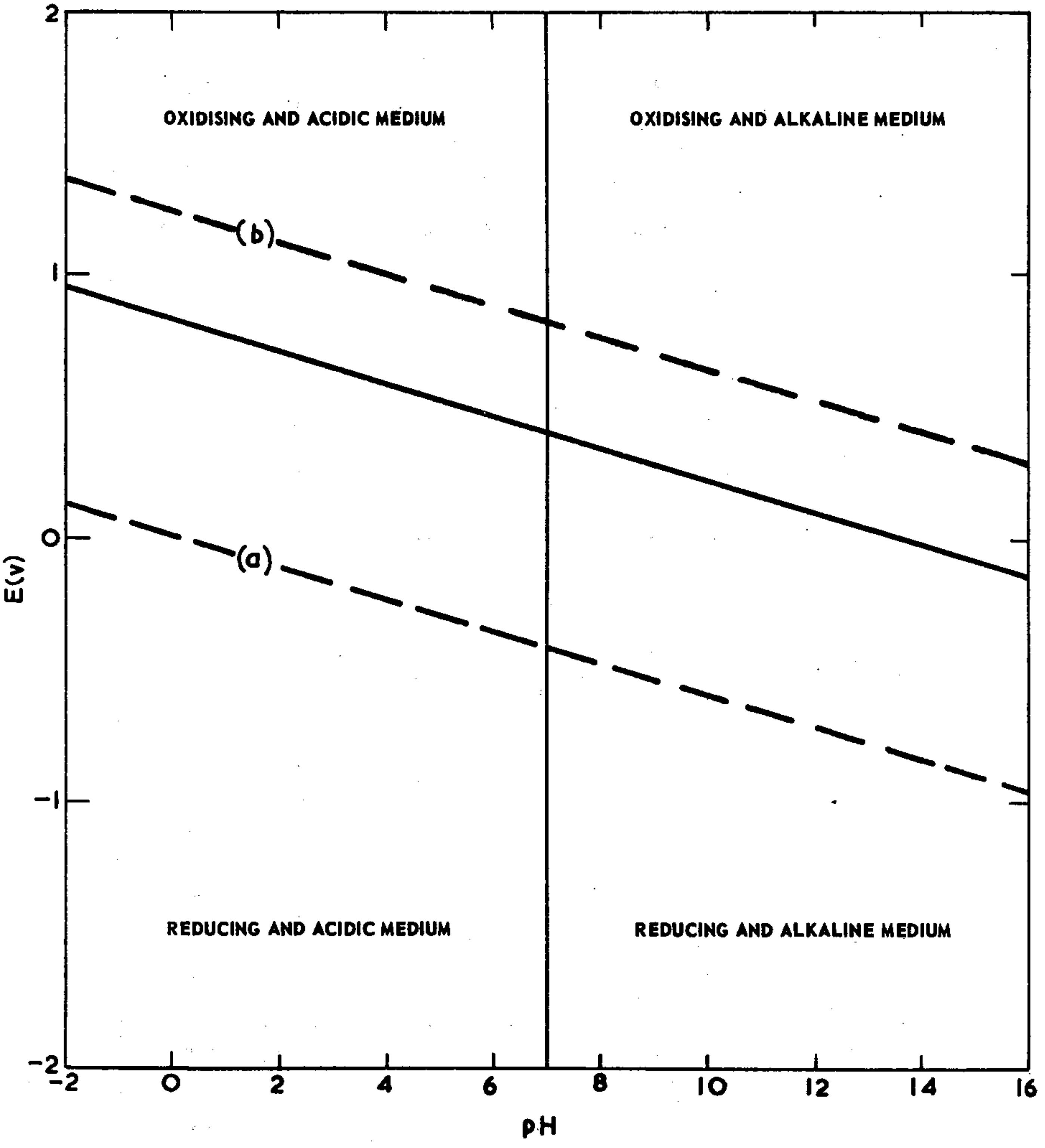

FIGURE 6a. ACID, ALKALINE, OXIDISING AND REDUCING MEDIA AT 298.16°K

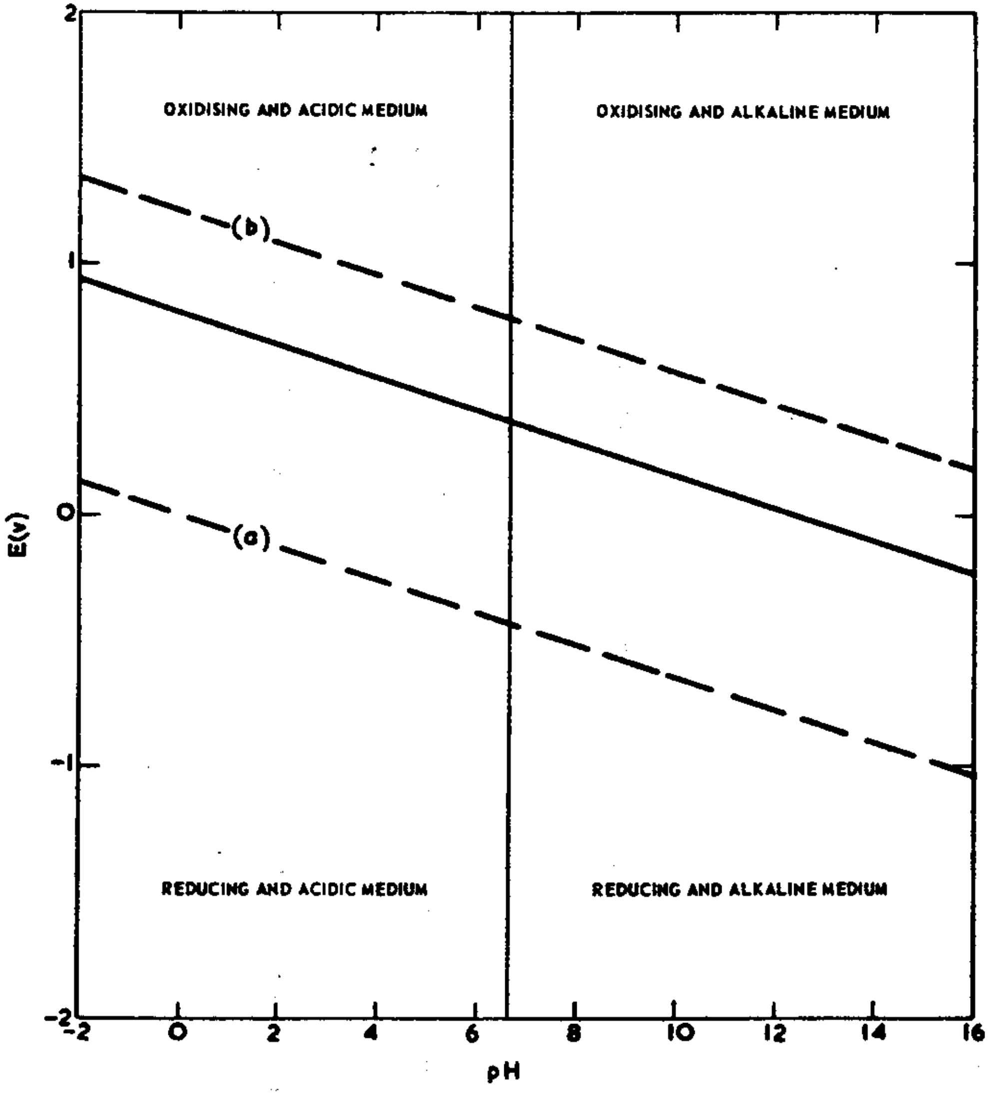

FIGURE 6b. ACID, ALKALINE, OXIDISING AND REDUCING MEDIA AT 323.16°K

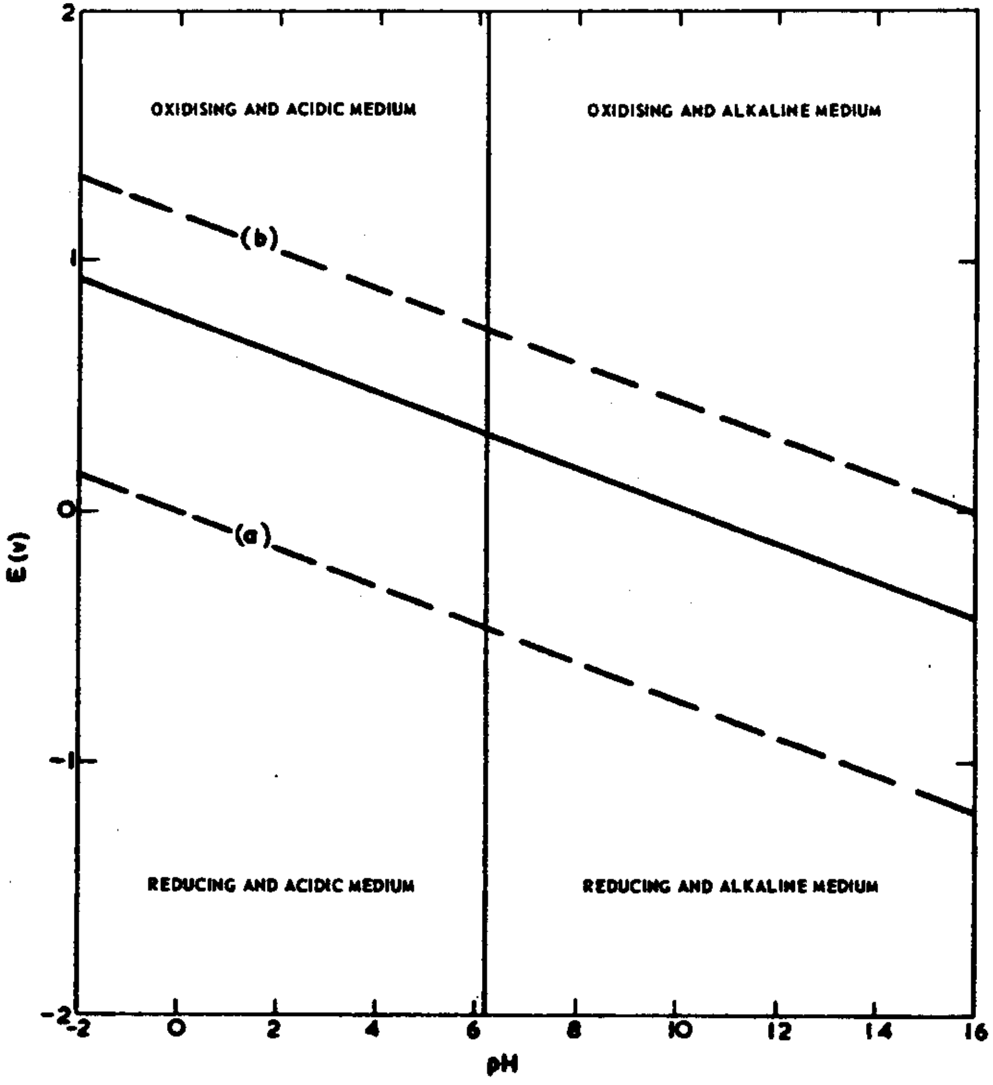

FIGURE 6c. ACID, ALKALINE, OXIDISING AND REDUCING MEDIA AT 373.16°K

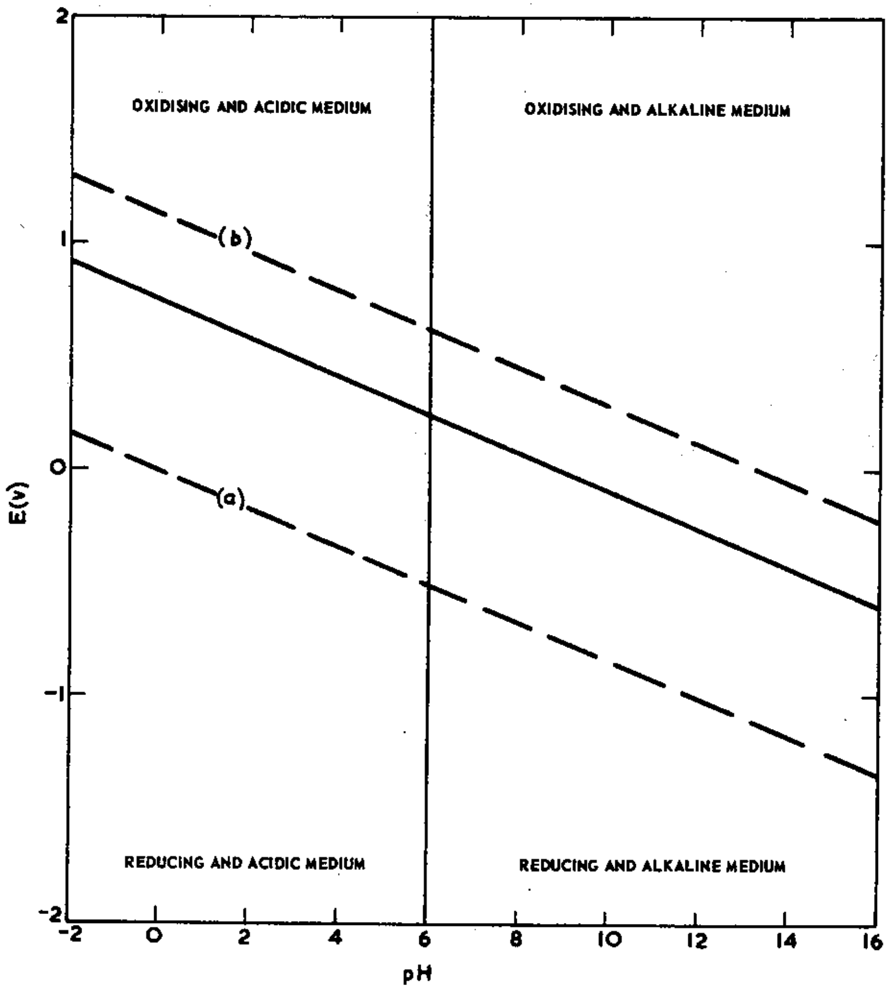

FIGURE 6d. ACID, ALKALINE, OXIDISING AND REDUCING MEDIA AT 423.16°K

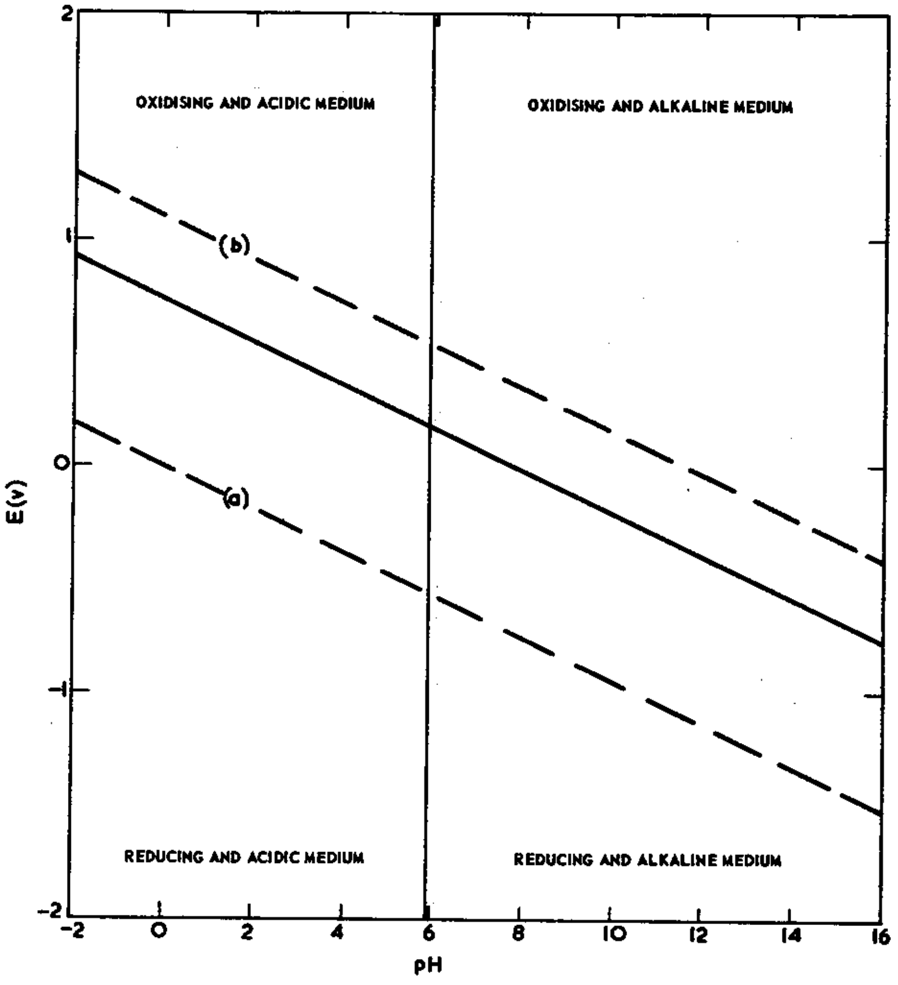

FIGURE 6e. ACID, ALKALINE, OXIDISING AND REDUCING MEDIA AT 473.16°K

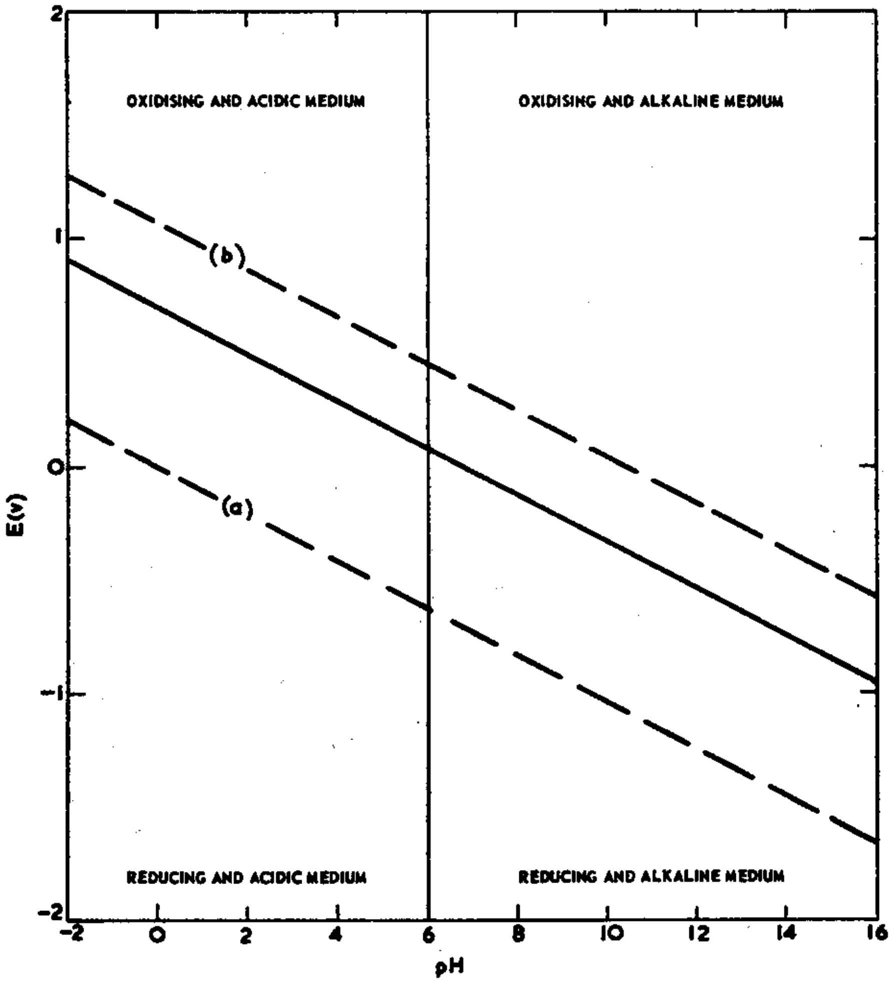

FIGURE 6f. ACID, ALKALINE, OXIDISING AND REDUCING MEDIA AT 523.16°K

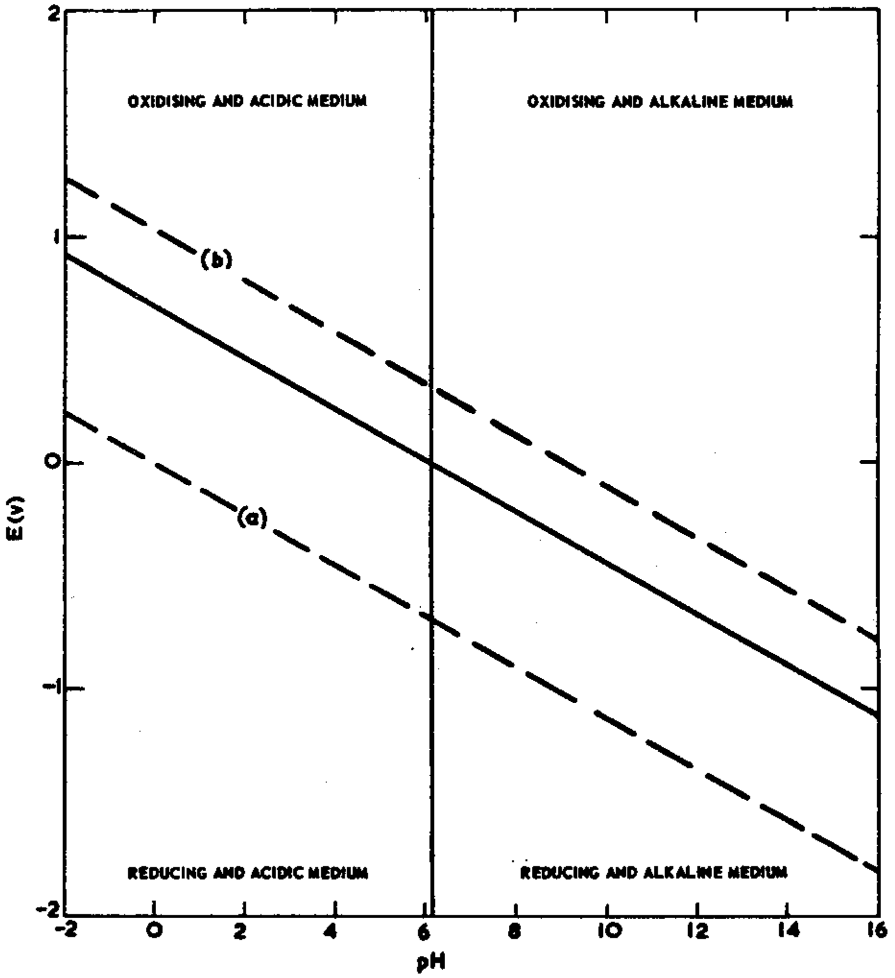

FIGURE 6g. ACID, ALKALINE, OXIDISING AND REDUCING MEDIA AT 573.16°K