

## FUEL CELLS—III. THE PROPYLENE POTENTIAL IN LOW TEMPERATURE CELLS\*

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**Abstract**—From the reproducible propylene potential observed at a platinum catalyst in 30% KOH solution, a potential of 0.465 V (NHE) at 25°C is calculated. The corresponding voltage for a propylene-oxygen cell is 0.838 V.

These values in conjunction with the observed temperature coefficient permit speculation regarding possible mechanisms and reactions in low-temperature propylene fuel cells.

**Résumé**—D'après des mesures reproductibles effectuées dans KOH 30% sur platine catalyseur, on propose une tension de 0,465 V à 25°C pour l'électrode à propylène (par rapport à E.N.H.). Cela correspond à 0,838 V pour une pile à combustible propylène-oxygène. Ces valeurs, ainsi que les coefficients de température qui s'y rattachent étayent certaines hypothèses sur les mécanismes des réactions dans les piles à propylène.

**Zusammenfassung**—Aus dem reproduzierbaren Propylenpotential, welches an einer Platin-Katalysator-Elektrode in 30% KOH-Lösung gemessen wurde, errechnet sich ein Potential von 0,465 V(NHE) bei 25°C. Die entsprechende Klemmenspannung einer Propylen-Sauerstoff-Zelle ist demzufolge 0,838 V.

Diese Werte, zusammen mit dem gemessenen Temperaturkoeffizienten, können als Ausgang für Vermutungen betreffend mögliche Mechanismen und Reaktionen in der Niedertemperatur-Propylenzelle dienen.

### INTRODUCTION

THERMODYNAMIC considerations are given in the present paper concerning the propylene potentials measured by the authors<sup>1</sup> in 30% potassium hydroxide solution *vs* a reference electrode of HgO in the same solution. Independent measurements<sup>2</sup> of such potentials at comparable temperatures and in comparable electrolytes, using a saturated calomel reference electrode and a different precious-metal catalyst, are in agreement to within 20 mV with those here considered.

On the basis of Niedrach's data,<sup>3</sup> the hydrogen content of the gaseous propylene used in the authors' experiments (Matheson C.P. Grade) is considered to be less than 0.0001 per cent by volume. For our present purpose one can only compare the experimentally measured voltage (criteria for the reversibility of which are given in the previous paper<sup>1</sup>) with the thermodynamically calculated voltage where every reaction proceeds under equilibrium and with good reversibility at standard conditions. Sign conventions throughout the present paper will be approached from the viewpoint of "oxidation potentials".<sup>4</sup>

### PROPYLENE POTENTIAL *vs* STANDARD HYDROGEN ELECTRODE

The data plotted on Fig. 12 of the previous paper<sup>1</sup> indicate that the potential,  $E_1$ , of the propylene electrode *vs* the HgO half-cell, and its temperature coefficient, are

$$E_1 = +0.59_2 \text{ V at } 25^\circ\text{C}, \quad (1)$$

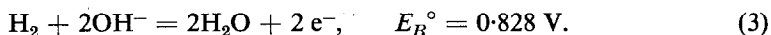
$$\frac{dE_1}{dT} = +2.3_3 \text{ mV}/^\circ\text{C}, \quad (20 \text{ to } 80^\circ\text{C}). \quad (2)$$

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The potential of the HgO *vs* hydrogen in the same solution at 25°C may be calculated as follows.

In alkaline solution, the half-cell reaction of hydrogen is



Thus, the Nernst expression for the potential of the half-cell can be written

$$E_2 = E_B^\circ - \frac{1.983 \times 10^{-4}}{2} T \log \frac{a_{\text{H}_2\text{O}}^2}{a_{\text{H}_2} \cdot a_{\text{OH}^-}^2}. \quad (4)$$

At 298°K and activity of hydrogen 1 at a pressure of 1 atm, the half-cell potential depends on the activities of water  $a_{\text{H}_2\text{O}}$ , and that of hydroxide ion,  $a_{\text{OH}^-}$ . No activity coefficient is available from the literature for  $\text{OH}^-$  in 30% KOH solution. Based on extrapolation of Harned's data,<sup>5</sup> the activity coefficient is estimated to be 3.0, resulting in  $a_{\text{OH}^-}$  being 21. The activity of water,  $a_{\text{H}_2\text{O}}$ , in the 30% KOH solution can be estimated as 49.9. Consequently, the half-cell potential *vs* normal hydrogen electrode and its temperature coefficient, are

$$E_2 = 0.80_6 \text{ V,} \quad (5)$$

$$\frac{dE_2}{dT} = -0.07_4 \text{ mV/}^\circ\text{K.} \quad (6)$$

The potentials of a HgO half-cell *vs* a hydrogen half-cell, in the same solution, were measured by Reuttschi<sup>6</sup> at temperatures of 25, 35 and 45°C and at KOH concentrations of 18.1, 26.0 and 34.7 per cent. His results indicate that the potential and temperature coefficient of a HgO half-cell *vs* a hydrogen half-cell in 30% KOH solution are

$$E_3 = -0.933 \text{ V,} \quad (7)$$

$$\frac{dE_3}{dT} = +0.24 \text{ mV/}^\circ\text{K.} \quad (8)$$

From (5) and (7), the potential of a HgO half-cell *vs* standard hydrogen electrode is

$$E_4 = -0.12_7 \text{ V.} \quad (9)$$

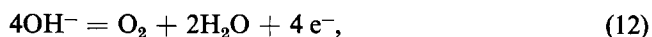
Consequently, the potential of propylene *vs* standard hydrogen electrode at 25°C is

$$E_5 = 0.59_2 - 0.12_7 = 0.46_5 \text{ V.} \quad (10)$$

From (2), (6) and (8), the temperature coefficient of the propylene potential *vs* the standard hydrogen electrode is

$$\frac{dE_5}{dT} = +2.5 \text{ mV/}^\circ\text{K.} \quad (11)$$

The following equations are available for the oxygen half-cell reaction in alkaline solution, when the water-oxygen couple is considered,



$$E_B^\circ = -0.401 \text{ V,}$$

$$E_6 = E_B^\circ - \frac{1.983 \times 10^{-4}}{4} T \log \frac{a_{\text{O}_2} \cdot a_{\text{H}_2\text{O}}^2}{a_{\text{OH}^-}^4}. \quad (13)$$

In 30% KOH solution, the oxygen potential at 1 atm *vs* standard hydrogen electrode, and the temperature coefficient of  $E_6$ , can be written,

$$E_6 = -0.37_3 \text{ V}, \quad (14)$$

$$\frac{dE_6}{dT} = +0.09_4 \text{ mV}/^\circ\text{K}. \quad (15)$$

The voltage and temperature coefficient for a propylene-oxygen cell can be obtained from (10) and (14), and (11) and (15), respectively,

$$E_7 = 0.83_8 \text{ V}, \quad (16)$$

$$\frac{dE_7}{dT} = +2.5_9 \text{ mV}/^\circ\text{K}. \quad (17)$$

The enthalpy change,  $\Delta H$ , for the cell reaction may be calculated by the use of the Gibbs-Helmholtz equation,

$$\Delta G - \Delta H = T \left[ \frac{\partial(\Delta G)}{\partial T} \right]_p \quad (18)$$

in which  $\Delta G$  indicates the free energy change. Since the free energy change is

$$\Delta G = -nE_7F \quad (19)$$

where  $n$  indicates the number of faradays of electricity for the reaction, the enthalpy change can be written,

$$\Delta H = -F \left[ nE_7 - T \left( \frac{\partial nE_7}{\partial T} \right)_p \right]. \quad (20)$$

If  $n$  is constant,

$$\Delta H = -nF \left[ E_7 - T \left( \frac{\partial E_7}{\partial T} \right)_p \right]. \quad (21)$$

By the introduction of (17) and (18),

$$\begin{aligned} \Delta H &= -nF(0.84 - 0.78) \\ &= -1.4 n \text{ Kcal.} \end{aligned} \quad (22)$$

This result indicates that the reaction in question may be endothermic. However, this conclusion depends on the difference between  $E_7$  and  $T(\partial E_7/\partial T)_p$ ; if the hydrogen-peroxide-oxygen couple is involved in the reaction of the oxygen half-cell,  $\Delta H$  becomes positive and exothermic. Generally, a positive sign for  $(\partial E/\partial T)_p$  implies an endothermic cell reaction.

## INFERENCE OF THE PROPYLENE ELECTRODE REACTION

The reaction of the propylene-oxygen cell can be considered from the viewpoint of comparing the cell voltage experimentally obtained,  $E_7 = 0.84$  V from (16) with the calculated voltage for various expected reactions. Standard free energy of formation for the compounds involved were taken from Lange's handbook; they are

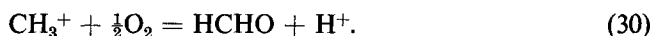
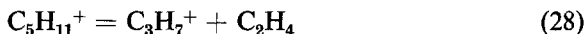
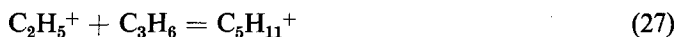
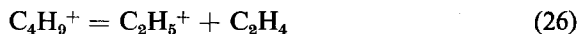
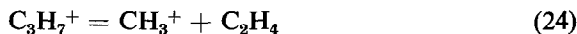
TABLE 1. PROPYLENE—OXYGEN CELL VOLTAGE AND NUMBER OF FARADAYS CALCULATED FOR DIFFERENT POSSIBLE REACTIONS

Reaction No.	Assumed Reaction	Number of faradays per mole $n$	Calculated cell voltage $E_7$ V
1	$C_3H_6 + \frac{1}{2} O_2 = \frac{2}{3} H_2CCH_2 + \frac{1}{3} HCHO$	0.67	0.13
2	$C_3H_6 + O_2 = H_2C(O)CH_2 + HCHO$	4	0.48
3	$C_3H_6 + O_2 = \frac{2}{3} H_2C(O)CH_2 + \frac{1}{3} HCOOH$	4	0.50
4	$C_3H_6 + \frac{1}{2} O_2 = H_2CCH_2 + HCHO$	2	0.54
5	$C_3H_6 + \frac{3}{2} O_2 = 3HCHO$	6	0.68
6	$C_3H_6 + \frac{1}{2} O_2 = \frac{2}{3} H_2CCH_2 + \frac{1}{3} HCOOH$	1.33	0.68
7	$C_3H_6 + \frac{3}{2} O_2 = H_2C(O)CH_2 + HCOOH$	6	0.73
8	$C_3H_6 + O_2 = H_2CCHCHO + HCHO$	4	0.79
9	$C_3H_6 + \frac{3}{2} O_2 + H_2O = CH_2OHCH_2OH + HCOOH$	66	0.85
10	$C_3H_6 + O_2 = H_2CCH_2 + HCOOH$	4	0.88
11	$C_3H_6 + O_2 = \frac{4}{3} CH_3CHO + \frac{1}{3} HCOOH$	4	0.92
12	$C_3H_6 + \frac{5}{4} O_2 = \frac{1}{2} H_2CCHCHO + \frac{1}{2} CH_3CHO + \frac{1}{2} HCOOH + \frac{1}{2} H_2O$	5	0.94
13	$C_3H_6 + \frac{3}{2} O_2 = CH_3CHO + HCOOH$	6	0.94
14	$C_3H_6 + 3 O_2 = 3HCOOH$	12	0.95
15	$C_3H_6 + O_2 = H_2CCHCHO + H_2O$	4	0.95
16	$C_3H_6 + 2 O_2 = \frac{1}{2} H_2CCHCHO = \frac{3}{2} HCOOH = \frac{1}{2} H_2O$	8	0.95
17	$C_3H_6 + O_2 = H_2CCH_2 + CO + H_2O$	4	0.96
18	$C_3H_6 + \frac{3}{2} O_2 = \frac{1}{2} H_2CCHCHO + \frac{1}{2} C_2H_5CHO + \frac{1}{2} H_2O$	3	0.98
19	$C_3H_6 + \frac{7}{2} O_2 = (COOH)_2 + HCOOH + H_2O$	14	0.99
20	$C_3H_6 + \frac{13}{2} O_2 = \frac{4}{3} (COOH)_2 + \frac{4}{3} H_2O + \frac{1}{3} HCOOH$	14.7	1.01
21	$C_3H_6 + 2 O_2 = CH_3COOH + HCOOH$	8	1.02
22	$C_3H_6 + \frac{3}{2} O_2 = CH_4 + 2 CO + H_2O$	6	1.04
23	$C_3H_6 + \frac{1}{2} O_2 = C_2H_5CHO$	2	1.06
24	$C_3H_6 + \frac{5}{2} O_2 = \frac{2}{3} CH_3COOH + \frac{1}{3} HCOOH$	6.67	1.07
25	$C_3H_6 + 2 O_2 = CH_3CHO + CO_2 + H_2O$	8	1.07
26	$C_3H_6 + 4 O_2 = 2 CO_2 + 2 H_2O + HCOOH$	16	1.08
27	$C_3H_6 + \frac{13}{3} O_2 = \frac{2}{3} CO_2 + \frac{2}{3} H_2O + \frac{1}{3} HCOOH$	17.3	1.11
28	$C_3H_6 + \frac{1}{2} O_2 = CH_3COCH_3$	2	1.13
29	$C_3H_6 + \frac{9}{2} O_2 = 3 CO_2 + 3 H_2O$	18	1.13
30	$C_3H_6 + O_2 = C_2H_5COOH$	4	1.15
31	$C_3H_6 + \frac{23}{4} O_2 + \frac{1}{7} H_2O = \frac{12}{7} C_2H_6 + \frac{12}{7} CH_4 + \frac{1}{7} CO_2$	2.47	1.45
32	$C_3H_6 + \frac{8}{14} O_2 + \frac{3}{7} H_2O = \frac{6}{7} C_3H_8 + \frac{6}{7} CO_2$	0.86	1.82

largely based on N.B.S. values cited by Rossini *et al.* For each reaction involving 1 mole of propylene, the number of faradays of electricity involved in the reaction,  $n$ , and the voltage calculated from  $n$  and  $-\Delta G$  are summarized in Table 1.

Ethylene, ethylene oxide, ethylene glycol, acetone, aldehydes (formaldehyde, acetaldehyde, propionaldehyde, acrolein), acids (formic, acetic, oxalic), carbon dioxide

and ethane are considered as reaction products. The following chain reaction is assumed in these given reactions. This involves the application of a hydrocarbon cracking theory in which the carbonium ion concept is introduced, following Greensfelders<sup>7</sup> and other workers,



In this case, the proton is supplied from a catalyst and the overall reaction,



is available if every reaction proceeds under quasi-equilibrium, with subsequent oxidation of the ethylene and formaldehyde produced.

According to the literature,<sup>8</sup> carbon dioxide (as carbonate) and a small amount of formic acid are found analytically in the alkaline electrolytes of hydrocarbon-oxygen cells operating near and below 200°C. However, the cell voltage calculated for the complete oxidation of propylene producing CO<sub>2</sub> and H<sub>2</sub>O (1.13 V) is much higher than the value obtained experimentally in the present work (0.84 V). For the production of CO<sub>2</sub>, H<sub>2</sub>O and formic acid (reactions 26 and 27 of Table 1), a voltage near to 1.1 V should be obtained. Considered only from the standpoint of the calculated voltages, formation of some combination of formaldehyde or formic acid with ethylene, ethylene glycol, oxalic acid or acetic acid would result in voltages closest to the experimental values.

According to one possible oxidation mechanism for alcohol,<sup>9</sup> the oxidation can be considered to proceed to an acid through aldehyde. In alkaline solution the acid produced is slowly oxidized to CO<sub>2</sub> and H<sub>2</sub>O. Hence, an oxidation of methanol produces four faradays for 1 mole of methanol. From this viewpoint, the aldehyde, ethylene glycol and ethylene may not be considered as final products determining the measured electromotive force. Some kinds of acid might be expected as the final products in question. However, this assumption is incompatible with the fact that CO<sub>2</sub> as carbonate is detectable analytically (the chemical decomposition of acids does not seem to be fast enough that the production of the CO<sub>2</sub> may be considered as due to other than an electrochemical oxidation of the acid).

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