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CO₂—Potentiometric Determination and Electrode Construction, a Hands-on Approach

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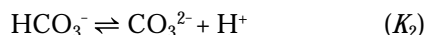
In an effort to improve science learning, we propose a practical approach, in which students build their own device to solve real-life problematic situations. In this way, interest, commitment, and concept acquisitions are increased. In the laboratory activity described here, students construct a simple but sensitive carbon dioxide detector. The device is a combination pH electrode with the addition of a gas-permeable membrane separated by a thin-film electrolyte solution (1, 2), as shown in Figure 1. Designing and building this device, using common and inexpensive laboratory materials, helps students in an undergraduate analytical chemistry course to understand some electrochemistry principles and their applications (3–5).

Carbon dioxide influences the shelf life, freshness, and taste of beverages. For this reason, we have students measure the carbon dioxide content of a common carbonated beverage. This procedure is a fundamental component of quality control systems and is used by almost all bottlers of soft drinks and mineral waters, as well as a number of breweries.

The prelab session includes a discussion of the principles of gaseous equilibria and electrochemical potentials. The laboratory work consists of the construction, calibration, and use of the carbon dioxide detector. A postlab class includes an analysis of the data and the application possibilities of the instrument. This last session also offers a biological rationale for the importance of monitoring gas content in yeast cultures under different growing conditions.

Prelab Session

The gas sensor electrode is constructed by adding a gas-permeable membrane to a pH electrode. A thin film of electrolyte solution is intercalated between the membrane and the electrode. When the gas diffuses across the membrane, it dissolves in the electrolyte solution, producing a pH change. The glass membrane electrode registers the pH variation, which can be used to determine the concentration of carbon dioxide in solution. The following equations explain this relationship. Carbon dioxide in aqueous solution presents the equilibria



The carbon dioxide of the sample diffuses across the membrane until concentrations on both sides of the membrane reach a reversible equilibrium (6). The charge balance of an aqueous sodium hydrogen carbonate solution is

$$[\text{Na}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HO}^-]$$

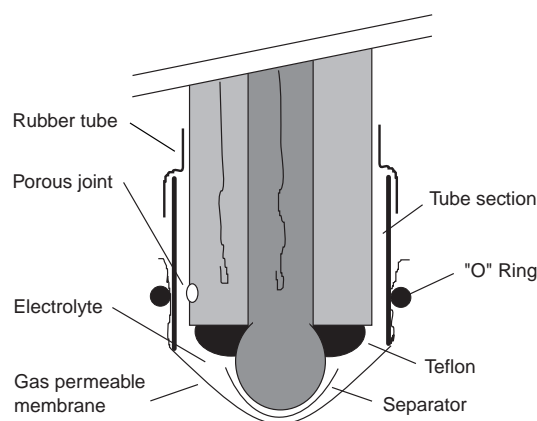


Figure 1. Detail of the sensitive area of the carbon dioxide electrode.

Substitution of the values in the charge balance by K_1 , K_2 and K_w gives

$$[\text{CO}_2] = \frac{[\text{H}^+]^2 + [\text{Na}^+][\text{H}^+] - K_w}{K_1 \left(1 + \frac{2K_2}{[\text{H}^+]} \right)} \quad (1)$$

If the sodium hydrogen carbonate concentration is in the range of 0.01–0.001 M, eq 1 can be simplified as described by Severinghaus (7):

$$[\text{CO}_2] = \frac{[\text{Na}^+][\text{H}^+]}{K_1}$$

Under these conditions, with a fixed sodium hydrogen carbonate concentration in the electrolyte chamber, $[\text{Na}^+]/K_1 = K'$ and

$$[\text{CO}_2] = K'[\text{H}^+]$$

$$\text{pCO}_2 = -\log K' + \text{pH}$$

From Bates (8), $E_H = -R'T \text{pH}$, where $R' = (R \ln 10)/F$, $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$, and $F = 96,487 \text{ C/equiv}$. Therefore

$$\Delta E = -R'T \Delta(\text{pH}) \quad (2)$$

Substituting for $\Delta(\text{pH})$ in eq 2 gives

$$\Delta E = -R'T \Delta(\text{pCO}_2) = -R'T \Delta(\log[\text{CO}_2]) \quad (3)$$

Therefore ΔE shows a linear response to changes in $\log[\text{CO}_2]$ due to CO_2 diffusion from the solution through

the membrane into the inner electrolyte solution. The equilibria involved in the outer solution are similar to those of the inner chamber of the sensor. Therefore the mass balance of the carbonate species is as follows:

$$[\text{CO}_3^{2-}(\text{tot})] = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

By substituting carbonic acid dissociation constants and rearranging the equation, the percentage fraction of carbon dioxide from total carbonate present in the solution becomes a function of pH:

$$\frac{[\text{CO}_2(\text{aq})] \times 100}{[\text{CO}_3^{2-}(\text{tot})]} = \frac{100}{\frac{1 + K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2}} = f$$

If pH = 5, then $f = 95.7\%$, and for more acidic pH values f approaches 100%.

Following Henry's law, the partial pressure of carbon dioxide is

$$[\text{CO}_2(\text{aq})] = k P_{\text{CO}_2}$$

$$P_{\text{CO}_2} = \frac{[\text{CO}_3^{2-}(\text{tot})] f}{k \times 100}$$

$$[\text{CO}_2(\text{aq})] = \frac{[\text{CO}_3^{2-}(\text{tot})] f}{100}$$

Therefore, substituting in eq 3 we find an equation that relates the total carbonates concentration with the sensor's response:

$$\Delta E = \frac{R T \Delta \left\{ \log \left(\left[\text{CO}_3^{2-}(\text{tot}) \right] f \right) \right\}}{100}$$

To maintain a constant f value, the pH of the outer solution should remain constant. In these conditions the following expression holds:

$$\Delta E = R T \Delta (\log [\text{CO}_3^{2-}(\text{tot})]) \quad (4a)$$

or

$$\Delta E = R T \Delta (\log P_{\text{CO}_2}) \quad (4b)$$

Practical Session

Materials and Methods

1. *Gas-permeable membrane.* Any hydrophobic membrane permeable to gases can be used. The students can make one with a silicone sealer (Silastic). The material is distributed carefully on a Teflon plate or Parafilm, forming a thin layer about 0.1 mm thick.
2. *A combination electrode.* This is used as a reference electrode and pH sensor.
3. *The electrolyte chamber.* It is made with "rice paper" (cigarette paper) 0.05 mm thick, soaked in hydrogen carbonate buffer solution. The paper is compressed between the silicone membrane and the electrode glass membrane. In this way a constant thickness (0.05 mm) of the chamber is achieved.

Table 1. Calibration Data for Hydrogen Carbonate Standard Solutions

Volume/mL		[CO ₂ (tot)]/ mol ⁻¹ L ⁻¹	pCO ₂	E/mV	ΔE/mV
Total	Standard				
55.0	0.0	—	—	-79.0	0.0
55.1	0.1	3.60 × 10 ⁻⁵	4.4437	-72.4	6.6
55.2	0.2	7.20 × 10 ⁻⁵	4.1427	-65.3	13.7
55.3	0.3	1.08 × 10 ⁻⁴	3.9666	-58.8	20.2
55.8	0.8	2.86 × 10 ⁻⁴	3.5436	-50.9	28.1
56.3	1.3	4.62 × 10 ⁻⁴	3.3354	-43.5	35.5
57.3	2.3	8.03 × 10 ⁻⁴	3.0953	-32.7	46.3
60.3	5.3	1.76 × 10 ⁻³	2.7550	-25.9	53.1

4. *Buffer solution.* This is used to fill the chamber. It is prepared by dissolving 1.17 g of sodium chloride and 0.42 g of sodium hydrogen carbonate in 1 L of distilled water.

5. *Solution used to adjust the ionic strength.* 1 M sodium citrate buffer, pH 5.0.

6. *Standard calibration solution.* 0.02 M sodium hydrogen carbonate.

7. *Thermostatic bath.* We used the one described by Mercer (9).

8. *Orion 701 pH meter.* Inner impedance >10¹² Ω. Used to measure E (mV).

9. *Other materials.* Teflon tape, disposable syringes of various volumes, O rings, thin "rice paper" (e.g., the one used for cigarettes), magnetic stirrer (optional).

Building the Electrolyte Chamber and Joining the Gas Electrode

A polyamide syringe, of an inside diameter slightly larger than the combination pH electrode, is cut to a length of 1.5 cm and the borders are sandpapered. The silicone membrane is fixed in one end of the syringe with an O ring. The opposite end is connected to the electrode by a rubber tube 1 cm long (Fig. 1). The combination electrode is carefully washed with the electrolyte solution and Teflon tape is rolled around the electrode neck to reduce the size of the chamber. A circle of rice paper 1 cm in diameter, soaked in electrolyte solution, is placed against the electrode. The electrolyte solution is added to the chamber and afterwards the electrode is introduced in it. The electrode's position is adjusted by straightening the silicone membrane. Once this has been done, the potential given by the electrode will change slowly until the potential corresponding to the carbon dioxide atmosphere concentration is reached.

Calibration with Sodium Hydrogen Carbonate Solutions

1. Place 50 mL of distilled water, a magnet rod, and 5 mL of ionic strength adjustment solution in a beaker.
2. Cover the beaker with Parafilm to avoid turbulence and place it in a stirring thermostatic bath.
3. Adjust the bath temperature to 30 ± 0.2 °C.
4. Introduce the CO₂ electrode through a hole in the Parafilm cover.
5. Start the electrode calibration by adding known volumes of the standard calibration solution.

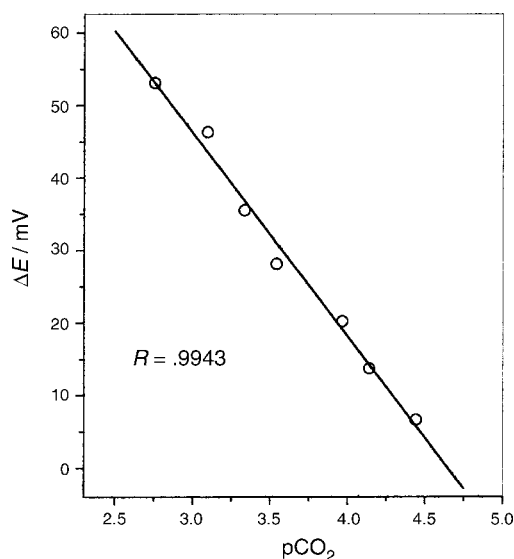


Figure 2. Calibration curve for hydrogen carbonate standards.

The data are shown in Table 1 and Figure 2. From the linear regression of these data we obtain the following equation ($r = .9943$):

$$\Delta E = -28.054 \times \text{pCO}_2 + 130.4 \quad (5)$$

From eq 5 the initial CO_2 concentration, before standard solution is added, is 2.2×10^{-5} M. This is in accordance with Murray's work (10). The data readings were taken after 3 min (Table 2). Response time characteristics are described elsewhere (11). We suggest the use of CO_2 solutions of concentration $\geq 10^{-4}$ M.

Determination of CO_2 in Soft Drinks

1. Pour 50 mL of distilled water and 5 mL of ionic strength adjustment solution into a beaker containing a stirrer. Record the initial reading (in millivolts) as mV_1 .
2. Add 0.5 mL of cold, recently opened beverage to the beaker. Record the new data as mV_2 .
3. Calculate $\Delta \text{mV} = \text{mV}_2 - \text{mV}_1$ and use the calibration curve (Fig. 2) to obtain the CO_2 concentration of the sample. Take into account that the dilution factor is 0.5:55.5. In cola can containers the CO_2 concentration is about 0.096 mol/L.

Postlab Session

After analysis of the construction and calibration of the instrument, the uses of the carbon dioxide detector should

Table 2. Time to Reach 90% of Equilibrium Value of Hydrogen Carbonate Standards

$[\text{CO}_2]/\text{M}$	Time/min
3.60×10^{-5}	5.5
7.20×10^{-5}	3.2
1.08×10^{-4}	2.0
2.86×10^{-4}	1.7
4.62×10^{-4}	0.3
8.03×10^{-4}	0.3

be discussed. For example, use the CO_2 electrode to analyze the metabolic rate of baker's yeast (*Saccharomyces cerevisiae*) at different pH values or substrate levels (12, 13). The applicable aspect of the constructed detector should be emphasized.

Conclusions

We have presented an interesting, low cost, hands-on activity for an analytical chemistry course. It has a prelab session where important electrochemical concepts are studied to provide the required background information for building a gas detector starting from a pH electrode. The laboratory part develops the students' manual skills and the application of general chemistry concepts in another context. It can easily be included in an interdisciplinary project involving physics, applied chemistry, or biology.

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