s_p	root mean square of differences between experimental pressure and pressure at the corresponding intersection of the perpendicular to the chord
s_T	root mean square of the difference between experimental temperature and temperature at the corresponding intersection of the perpendicular to the chord
t	temperature, °C
T	temperature, K
T_{mn}	temperature of transition from state *m* to state *n*, K
T_x	triple point temperature, K
z	perpendicular distance to chord along equation; function to be treated by least-squares fitting
Z	compressibility factor
δp	the greater of 0.1 Torr or 0.0002 *p*; estimated uncertainty in pressure measurement
δT	0.1 K; estimated uncertainty in temperature of apparatus
ΔH_{mn}	enthalpy change from state *m* to state *n*, kcal mol^{-1}
ΔS_{mn}	entropy change from state *m* to state *n*, cal deg^{-1} mol^{-1}
σ	standard deviation

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Standard Potential of the Mercury–Mercurous Benzoate Electrode at 20 °C

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The standard potential of the mercury–mercurous benzoate electrode has been determined to be 430.64 ± 0.09 mV in aqueous benzoic acid solutions at 20 °C. The standard potential between 20 and 40 °C is given to within ±0.1 mV by the expression $E^\circ = 0.4480 - (945.7 \times 10^{-6})t + (3.429 \times 10^{-6})t^2$.

Mercury–mercurous carboxylate electrodes have aroused considerable interest recently as possible internal reference electrodes for ion-selective electrodes (*3*). As part of a systematic study of these carboxylate electrodes we report the results of our investigation of the mercury–mercurous benzoate electrode. This electrode had been investigated previously from 25 to 40 °C by Bertram and Bone (*1*) and at 25 °C by Chauchard and Gauthier (*2*). In these prior investigations classical paste electrodes had been used. In this study the skin-type electrode described by Hills and Ives (*4*) for the calomel electrode which led to the improvement in performance of that electrode was used.

Electromotive force measurements of the cell of the type $Pt|Q{\cdot}QH_2|HBz(m)|Hg_2Bz_2|Hg$ have been made at 20 °C. The acid concentrations ranged from 0.005 to 0.015 mol kg^{-1}. The standard potential was computed from a thermodynamic analysis of the data.

Experimental Section

Mercurous benzoate was prepared and stored as described by Bertram and Bone (*1*). Mercury was triple distilled and was purified by the method of Hills and Ives (*4*). Fisher reagent grade quinhydrone was recrystallized from conductivity water acidified with benzoic acid (pH 5) and stored in a desiccator over quinone in the dark. Baker Primary Standard benzoic acid was used as received. Benzoic acid solutions were made up volumetrically and weighed aliquots titrated with carbonate-free standardized sodium hydroxide. Oxygen was excluded during all preparations and procedures through the use of nitrogen.

The electrode cell compartments were similar to those used by Larson and MacDougall for the mercury–mercurous acetate electrodes (*7*) and were arranged similarly. The mercurous benzoate cells were rendered hydrophobic by treatment with Clay Adams wetting solution and the quinhydrone cells were painted black. Electrodes for the quinhydrone half-cells were of platinum wire (22 gauge) sealed in soft glass tubing (*9*).

The mercury–mercurous benzoate cell solution was prepared by stirring a deaerated benzoic acid solution, mercurous benzoate, and mercury for 72 h in the dark under nitrogen. The mercurous benzoate skin was prepared by shaking mercury and mercurous benzoate in a small flask and adding both mercury and skin to a clean mercury surface in the cell compartment. The previously stirred cell solution was added. Quinhydrone electrodes were prepared by adding quinhydrone twice washed with cell solution to deaerated benzoic acid. Three electrodes of each type which agreed to 0.05 mV were made for each run and three runs were made for each concentration. The thermostat was a transformer oil bath. Temperature control was to 0.02 °C and the temperature was verified with an NBS calibrated thermometer.

Table I. Electromotive Force Measurements

m/mol kg^{-1}	$(m - m_{H^+})$/ mol kg^{-1}	E/V
0.005 931	0.005 353	0.102 37
0.009 622	0.008 878	0.088 45
0.013 322	0.012 441	0.078 86
0.014 066	0.013 160	0.077 44

Emf measurements were made using a Keithley 662 guarded differential voltmeter enabling the emf to be read to 0.001 mV. All cells reached equilibrium within an hour. The equilibrium emf was constant to 0.05 mV for 4 h after which readings were discontinued.

Theory

For the cell given the cell reaction is

$$Hg_2Bz_2 + QH_2 = 2Hg + Q + 2H^+ + 2Bz^-$$

The emf is given by

$$E = E^\circ_{Hg|Hg_2Bz_2} - E^\circ_{Q|QH_2} - RT/F \ln a_{H^+}a_{Bz^-} \qquad (1)$$

For the dissociation of benzoic acid

$$HBz = H^+ + Bz^- \qquad (2)$$

we have

$$K = a_{H^+}a_{Bz^-}/a_{HBz} \qquad (3)$$

where

$$a_{HBz} = m_{HBz}\gamma_{HBz} \qquad (4)$$

We calculate m_{HBz} by the method of Bertram and Bone (*1*)

$$m_{HBz}(\text{undissociated}) = m_{HBz}(\text{stoichiometric}) - m_{H^+}$$

and

$$m_{H^+} = (Km_{HBz})^{1/2}$$

Substituting for the product of ionic activities in eq 1 from eq 3 and 4 we obtain

$$E = E^\circ_{Hg|Hg_2Bz_2} - E^\circ_{Q|QH_2} - RT/F \ln Km_{HBz}\gamma_{HBz}$$

A plot of $E + E^\circ_{Q|QH_2} + RT/F \ln Km_{HBz}$ (= $E_m^{\circ\prime}$) against the molality of undissociated benzoic acid has an intercept equal to $E_m{}^\circ{}_{Hg|Hg_2Bz_2}$.

Results and Discussion

In Table I are the results obtained. In Figure 1 is plotted $E_m^{\circ\prime}$ calculated according to the final expression in the theory. The value of E_m° for the quinhydrone electrode, 0.70334 V, is taken from Janz and Ives (*5*); the dissociation constant of benzoic acid is from Jones and Parton (*6*). The values of the constants were from Robinson and Stokes (*8*). The E_m° value found is 430.64 ± 0.09 mV (20 °C).

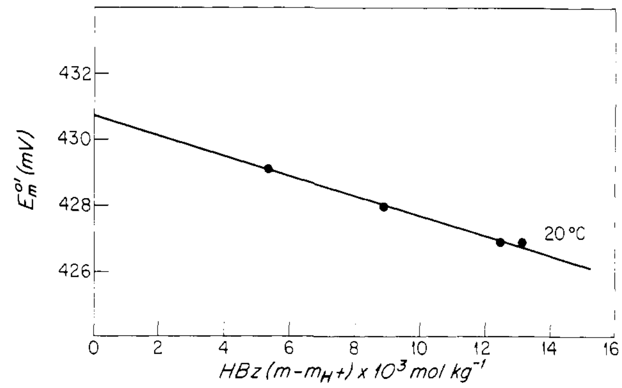

Figure 1. Variation of $E_m^{\circ\prime}$ with benzoic acid concentration.

Table II. Standard Potentials of the Mercury-Mercurous Benzoate Electrode

Temp, °C	E°, V	Temp, °C	E°, V
20	0.4306	35	0.4193
25	0.4263	40	0.4156
30	0.4228		

The results of Bertram and Bone (*1*) and of this research are presented in Table II. They are represented to within ±0.1 mV by the expression

$$E^\circ = 0.4480 - (945.7 \times 10^{-6})t + (3.429 \times 10^{-6})t^2$$

where t is the temperature in °C and potentials are in absolute volts.

Mercury-mercurous salt electrodes when properly prepared and equilibrated (*4*) can serve as a class of reproducible reference electrodes in various solvents.

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