Studies on the Polarographic Analysis. XI. New Differential Polarography with One Dropping Electrode⁽¹⁾

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Introduction

With the progress of polarography, interest in the differential technique has recently been aroused by Heyrovsky⁽²⁾ and other workers.⁽³⁾ Their methods depend on the use of two mercury electrodes dropping at the same rate, but this manipulation is very difficult. It was tried to make the drops fall at regular intervals by magnetic force or to make use of a streaming electrode and yet little has been gained in practice.

Delahay deviced to differentiate the electrometric titration curves with regard to time by inserting a condensor in series with a recording galvanometer and Lévèque and Roth have recently applied the method for differentiating the polarographic curves.⁽⁴⁾ According to their method, therefore, the differential current can not be measured at any moment while the increase of the applied potential is stopped and also a good reproducibility is scarecely expected because of the use of an electrolytic condensor of a large capacity.

According to the authors' method, in which a rotating current-alternator similar to that of the Kalousek's method is used,⁽⁵⁾ two applied potentials different by ΔE are applied by turns and the corresponding electrolytic currents flow through a galvanometer alternatively in reverse directions. Therefore, the differential current with one dropping electrode is easily measured at any applied potential and moreover, when the rotation of the current-alternator is stopped, it comes back to an ordinary polarograph without changing the circuit. These are the differences arising from the use of above mentioned methods.

In conclusion, however, the differential curves obtained by the authors' method show maetrially the differential curve of the ordinary polarogram only when the electrode reaction takes place so rapidly that the diffusion is a rate determinant and also when the reaction is irreversible. On the other hand they take on some different aspects in case of a reversible reaction or of a slow reaction rate.

Instrumentation

As seen from the circuit shown in Fig. 1, when potentiometer drum R and sliding contact C are used, potential difference between A and C, *i. e.*, E volt is applied to the cell and by inserting two resistances R_1 and R_2 in parallel with R and connecting B with anode, potential difference between B and C *i. e.*, $E-\Delta E$ volt is applied to the cell. Hence, if a four-poles-double-throw switch and a galvanometer are connected between A, B and the anode as indicated in the figure, a normal polarogram can be obtained when the switch is settled in side "norm.", while a polarogram in which the voltage is consecutively less by ΔE than in the former polarogram is obtained in the contrary direction when the switch is settled in one's turn in side "rev.", so the latter is $E-\Delta E$ *vs.* $-i'$ curve (Curve 2 in Fig. 3). Therefore the galvanometer will indicate $(i-i'/2)=\Delta i$ provided that the changing of the switch connection to side "norm." or "rev." is performed alternatively in regular intervals and moreover, so rapidly as the the galvanometer cannot correspond with the changing of currents because of its

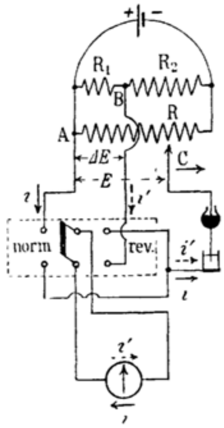

Fig. 1.—The principle of the differential polarograph.

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(1) Presented at the annual meeting of the Chemical Society of Japan in 1951.

(2) J. Heyrovsky, *Chem. Listy*, **40**, 222 (1946).

(3) G. Semerano and L. Riccoboni, *Gazz. Chim. ital.*, **72**, 297 (1942).

(4) P. Lévèque and F. Roth, *J. Chim. Physique*, **46**, 480 (1949).

(5) M. Kalousek, Collection *Czech. Chem. Communs.*, **13**, 105 (1948).

inertia. In consequence of this, a differential polarogram, E *vs.* $\Delta i/\Delta E$ curve (Curve 3 in Fig. 3) should be obtained by sliding C continuously along R as in case of an ordinary polarography. To make in practice the connection change of the switch so rapid and at regular intervals, a cylindrical rotating switch shown in Fig. 2 is used and the rotation velocity is well adjusted at any interval from 500 to 1,500 r. p. m. Though this rotation velocity of the cylinder is influenced by characteristic properties of galvanometer, 700 to 1,000 r. p. m, is usually adopted (about four times faster than the Kalousek's experiment) and we can carry out the works with much reproducibilities even without using a synchronous motor.

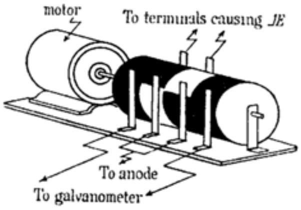


Fig. 2.—The rotating-current-alternator (the differentiator).

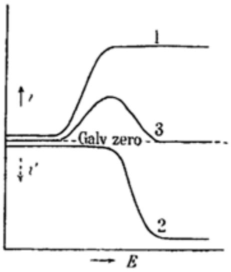


Fig. 3.—Schematic representation of the differential wave: curve 1, normal wave ($E\sim i$ curve); curve 2, reverse wave ($E-\Delta E\sim -i'$ curve); curve 3, composite differential wave ($E\sim\Delta i/\Delta E$ curve).

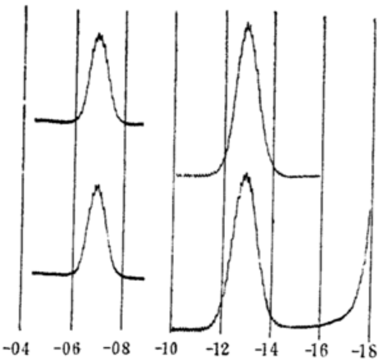


Fig. 4. — Reproducibility of the differential polarograms: left waves, Cd^{++} in KCl; right waves, Zn^{++} in NH_4Cl-NH_4OH.

Results Obtained and Discussions

On the Reproducibility.—If ΔE is always fixed and there is not a large fluctuation in the rotation velocity, the results of a good reproducibility can be easily obtained. Fig. 4 indicates the reproducibility of the differential polarograms as for cadmium in chloride solution and as for zinc ammine solution.

On the Relation between the Peak Potential (E_h) of Differential Curve and the Half-Wave Potential ($E_{1/2}$) of Ordinary Curve.—The polarogram of simple metal ion is formulated as below by Heyrovsky and Ilkovic;

$$E=E_{1/2}-RT/nF\cdot[\ln i/(i_d-i)] \qquad (1)$$

where E is potential of dropping electrode, $E_{1/2}$ half-wave potential, i electrolytic current corresponding to E, and i_d diffusion current. Here

$$i=i_d/e^{nF(E-E_{1/2})/RT}+1 \qquad . \qquad (2)$$

Hence, differentiating current i with regard to applied potential E, we get

$$\mathrm{d}i/\mathrm{d}E=-\frac{nF/RT\cdot i_d\cdot e^{nF(E-E_{1/2})/RT}}{\{e^{nF(E-E_{1/2})/RT}+1\}^2} \qquad (3)$$

Suppose $\mathrm{d}^2i/\mathrm{d}E^2$ to be zero, then $E=E_{1/2}$. Hence, from the formula (3) we get

$$(\mathrm{d}i/\mathrm{d}E)_{E=E1/2}=-nF\cdot i_d/4RT \qquad (4)$$

So, let E be negative, the differential curve indicates its maximum value at $E_{1/2}$, which is denoted by $nF\cdot i_d/4RT$.

However, the formula (3) is only approximately effective even though ΔE is taken small enough and also the electrode reaction does not always take place fundamentally in accordance with the formala (1), it may be admitted that the peak potential of differential curve is not necessarily in accord with the half-wave potential, But taking $E-\Delta E/2$ instead of E for the potential axis, we can see usually a good accordance of them. (see Table 1). Accordingly, the precise half-wave potential is possible to be measured in qualitative analysis when ΔE is taken small enough.

On the Separability.—In the ordinary polarogram, the half-wave potential is generally on a gentle slope which is apt to give a cause for the overlap of two neighboring waves.

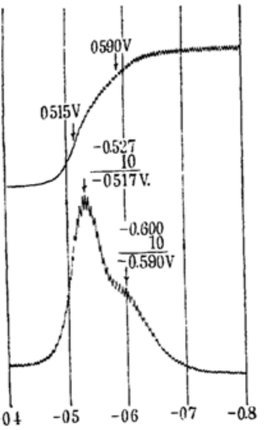
Table 1

Peak Potentials (E_h) and Half-Wave Potentials ($E_{1/2}$)

sample	ΔE, mV.	$Eh=E-\Delta E/2$ (vs. S.C.E.), V.		$E_{1/2}$ (vs. (S.C.E.),V.
Cd^{++} in KCl	20	-0.64_2,	-0.66_5*	-0.64_2
	40	-0.64_4		
	54	-0.64_4		
	54	-0.64_4		
	98	-0.64_6		
	206	-0.65_4		
Zn^{++} in NH_4OH	20	−1.36,	−1.38*	−1.36
	54		−1.38*	
	98		−1.39*	
	206		−1.36*	

* With damped galvanometer

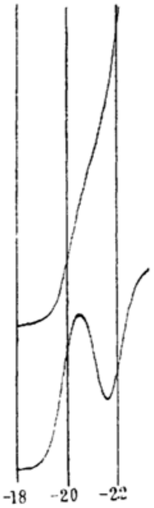
While in the differential polarogram the half-wave potential is denoted by the potential which gives the maximum value of the curve, Moreover, according to this method, the increase in the current often occurs at maximum part owing to the dissolution of the deposited metals and the decrease of it after the maximum takes place by the stoppage of the dissolution phenomena and the minimum between two neighboring maximum is deeply notched. Hence in many cases it is possible to separate the waves whose difference is only 75 millivolts. This availability is more clearly observed particularly in separation at the last increasing domain (Fig. 5 and Fig. 6).



Applied potential, volt

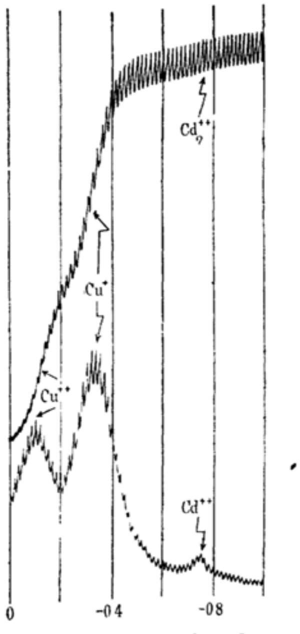
Fig. 5.—Separability of the neighboring waves. Pb^{++} and Tl^{+} in 0.1 N KCl—0.1 N HNO_3: curve 1, ordinary curve; curve 2, differential curve (ΔE=20 mV.).

On the Elimination of the Components of the Diffusion Current and of the Residual Current.—The effect of the diffusion current is eliminated, so the imperfect detection and determination in the normal polarogram when much formerly discharging matters are present together are quite excluded or considerably lessened and that the sensitivity of the galvanometer is fairly magnifiied. The result of the experiment is shown in Fig. 7. In the



Applied potential, volt

Fig. 6.—Separability of the neighboring waves. Impurities in crude LiCl: curve 1, ordinary curve; curve 2, differential curve (ΔE=50 mV.).



Applied potential, volt

Fig. 7.—Polarograms of brass dissolved in ammoniacal solution: curve 1, ordinary curve; curve 2, differential curve.

next place as for the residual current, it does not give much interference in the differential polarogram, since it always indicates the constant value. Therefore, the detection of the minute component is well carried out, which is inclined to be obstructed by the comparatively great residual current.

On the Elimination of the Current Vibration.—The current vibration caused by dropping of mercury drops is one of the factors which makes the measurements obscure in the normal polarogram. However, in the authors' differentical method this phenomena should be theoretically excluded; if the potential difference $\varDelta E$ is enough infinitesimal. At any moment two reverse currents, which are yielded one after another, cancel themselves mutually in the domain of the diffusion current, namely in part excluding the peak in the differencial polarogram. (By the way this elimination does not take place in the Lévèque's method). In practice, however, the vibration is seen all the same in the part of the peak and larger the potential difference is, the larger the vibration becomes. (See also Fig. 7).

Summary

The authors studied on the new differential polarography; its instrumentation and result obtained were particularly reported in the present paper. Discussions for its quantitative analysis and for the electrode reactions and some utilities of current-alternator will be followed.

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