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APPARATUS FOR A ROTATING DISC ELECTRODE

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Since Levich¹ developed the theory of convective diffusion as applied to a disc rotating in a solution, the rotating disc electrode has been very widely employed in physico-chemical research — in determining the concentration and the diffusion coefficients of solutes, studying the kinetics of electrochemical processes, the dissolution of a solid in a liquid, some homogeneous chemical processes, etc.²⁻⁶

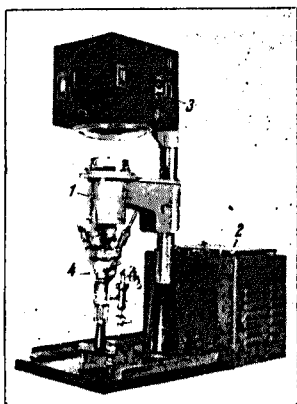


Fig. 1. General view of apparatus with rotating electrode: 1) electric motor; 2) electronic generator; 3) stroboscopic tachometer; 4) electrochemical cell.

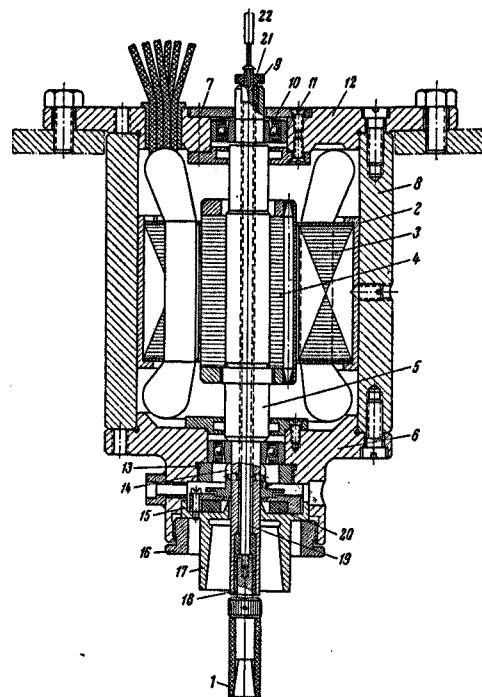


Fig. 2. High-frequency electric motor; 1) electrode; 2) stator frame; 3) stator laminations; 4) rotor laminations; 5) rotor shaft; 6) lower cover; 7) collar; 8) housing; 9) spindle; 10) spring; 11) bearing; 12) upper cover; 13) nut; 14) coupling; 15) copper-graphite ring; 16) nut; 17) cone; 18) insulating coupling; 19) insulating tube; 20) elastic member; 21) insulating coupling; 22) copper-graphite needle

In several cases measurements must be carried out under conditions ensuring a rapid transfer of a reactant from the bulk of the solution to the electrode surface (while laminar flow of the liquid is maintained), which is achieved by increasing the rate of rotation of the disc. Arrangements involving a rotating electrode described in the literature^{2,7} allow rates of rotation of 20 000–22 000 rev/min to be attained. They possess several design defects, and are inconvenient to operate (there is no smooth adjustment of rate of rotation, prolonged measurements at a high rate of rotation are impossible, etc.). The laboratory set-up described below is free from these defects, and enables electrochemical processes to be studied under conditions of vigorous mixing of the solution. The rate of rotation of the electrode can be changed smoothly over the range 900–33 000 rev/min; it remains stable to within $\pm 1\%$ of the nominal value.

The apparatus is mounted on a bench stand (Fig. 1) and comprises the following parts:

1. A high-frequency electric motor with a vertical shaft, to the lower end of which is fixed the electrode.
2. An electronic generator to start the motor.
3. A PST-1 stroboscopic tachometer to measure the rate of rotation.
4. The electrochemical cell.

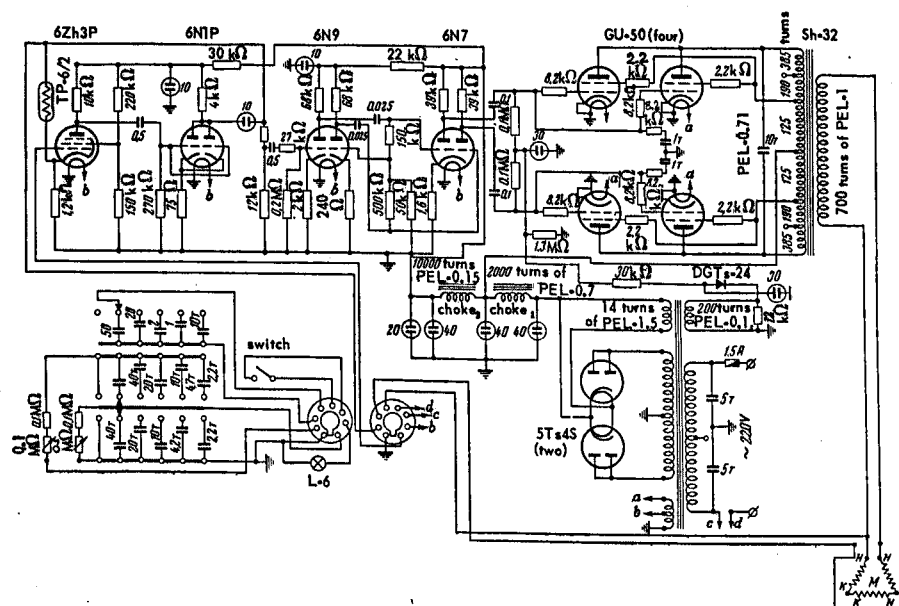


Fig. 3. Circuit of electronic generator [International valve equivalents: 6Zh3P - 6AG5; 6N1P - no equivalent; 6N9 - probably 6SL7; 6N7 = 6N7; GU-50 - LS50; 5T45 - 5Z4. The units of capacity used here are obscure (Ed. of Translation)].

Electric Motor

The drive is provided by a high-frequency, short-circuited, asynchronous, three-phase 0.05 kW electric motor (Fig. 2). The stator 3 of the motor is composed of laminations 0.35 mm thick of E-44 steel for electrical-engineering purposes. The number of slots z_1 is 12. The winding of the stator consists of two layers of PEV-2 wire.

The core of the stator is placed within the housing 8, which is a hollow cylinder to both ends of which are fixed cover plates 6 and 12 containing the bearings 11. The centring of the stator and the end plates on the same surface avoids the formation of an appreciably crescent-shaped air gap between the rotor and the stator; this is necessary if the motor is to operate at high speeds without vibration.

The rotor shaft 5 is supported by TsKB-667 radial-thrust ballbearings having a diameter fitting a shaft of 9 mm. They have a so-called "key" on the inner ballrace and a cage round the edges of the outer ballrace. The initial interference fit of the bearings, necessary for normal operation of the motor, is provided by the spring 10 at a tension of 2-3 kg. The rotor of the motor consists of iron laminations and a "squirrel cage". The number of bars z_2 is 10.

Electronic Generator

The electric motor is fed from a 0.1 kW electronic power generator. The rate of rotation of the rotor of the electric motor is changed by varying the frequency of the generator between 15 and 550 c/s. The generator comprises a master oscillator, a preliminary amplification

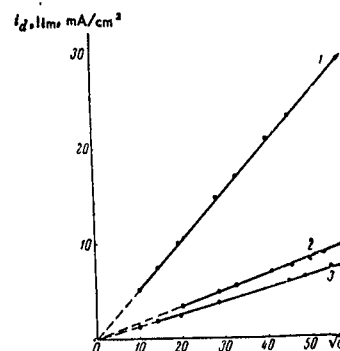


Fig. 4. Dependence of the limiting current on the angular velocity of rotation of the electrode: 1) reduction of KMnO_4 (1.5×10^{-3} M) at a gold electrode; 2) oxidation of quinol (1.73×10^{-3} M) at a gold electrode; 3) reduction of $\text{K}_2\text{Cr}_2\text{O}_7$ (3.31×10^{-4} M) at an amalgamated gold electrode. Supporting electrolyte - NH_4SO_4 .

stage, a final stage, a supply unit, and a set of capacitors for the phase shift in the motor winding (Fig. 3).

The master oscillator operates on 6Zh3P and 6N1P valves in a two-stage RC circuit. The parameters of the frequency-selection quadripole in the positive feedback circuit are calculated for frequencies of 15-550 c/s. This range is divided into four bands, stepwise adjustment of the

frequency being achieved by switching in the capacitances of the frequency-selection quadripole*, and continuous adjustment by means of a duplicate variable resistance.

The phase-reversal stage operates with a 6N9 valve in a self-balancing circuit, and the pre-power stage with a 6N7 valve in a paraphase circuit. The final stage consists of a two-step ultralinear circuit with two GU-50 valves in each arm. To correct the frequency characteristic of the amplifier, the control grids of the GU-50 valves are shunted with resistances and capacitances. The primary winding of the output transformer also is shunted with capacitances.

The generator is supplied from a.c. mains through a full-wave kenotron rectifier assembled from 5Ts4S valves, the rectified current being smoothed by means of a two-unit filter.

Electrode and Sealing Arrangement (Fig. 2)

The electrode 1 is a steel rod, to which is fixed a truncated cone of the metal under investigation. The working surface is the lower base of the cone of diameter 6.5 mm, the lateral surface of the electrode being coated with Teflon. Several interchangeable electrodes can be made for the apparatus**. The electrode is fixed to the rotor shaft 5 by means of an insulating coupling 18, vertical movement being prevented by the spindle 9, which passes through the rotor shaft and is insulated from it by the polyvinyl chloride tube 19 and the couplings 18 and 21. Current is conducted to the electrode by means of a sliding contact formed by the upper end of the spindle 9, into which is pressed a platinum cap, and a copper-graphite needle 22, placed in line with the axis of the shaft and fixed to the housing of the motor. The resistance of the contact does not exceed a few tenths of an ohm.

The electrochemical cell is placed under the motor and is fixed to the cone 17 by a ground-glass joint. The cell is made airtight during rotation of the electrode by means of a flanged brass coupling 14 attached to the shaft and the fixed copper-graphite ring 15, placed over the cone 17. The ring 15 is pressed against the coupling 14 by the elastic member 20 made of rubber sponge. The gaps between the coupling 14 and the shaft 5 and between the ring 15, the cone 17, and the elastic member 20 are sealed with varnish.

EXPERIMENTAL

The limiting diffusion current at a rotating disc electrode is given by the expression¹

$$i_d = 0.62 n F D^{1/2} \nu^{-1/2} \omega^{1/2} c$$

where n is the number of electrons taking part in the process, F is the Faraday, ν the kinematic viscosity of the solution, D the diffusion coefficient of the substance which reacts at the electrode, c its concentration, and ω the angular velocity of the electrode ($\omega = 2\pi m$, where m is the number of rotations of the electrode per second). The above formula is correct for laminar flow of the liquid (Reynolds number $1 \ll \text{Re} < 10^5$).

* When the bands are changed over, the capacitances also are changed over to produce a phase shift in the motor winding.

** When it is necessary to carry out measurements under conditions of turbulent flow of the liquid, an electrode which is not streamlined in shape must be used.

Fig. 4 shows the relation between the limiting current i_d and $\sqrt{\omega}$ for various oxidation and reduction reactions. Direct proportionality between these quantities is maintained, for the reduction of $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 and the oxidation of quinol, over the whole range of ω investigated (Reynolds numbers between 10^3 and 4×10^4), which confirms that the motion of the liquid remains laminar up to 33 000 rev/min in this apparatus.

We express our gratitude to V.S. Batrukov, who designed the electrode and the sealing arrangement.

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D. S. KORZHINSKII'S PAPER ON "CRITICAL STATES IN SYSTEMS WITH FULLY MOBILE COMPONENTS"¹

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I feel I must make the following comments on Korzhinskii's paper¹:

1. The author¹ writes (pp. 1536–1537): "The problem of temperature and pressure maxima and minima was considered by Gibbs and Konovalov for binary systems. The Gibbs–Konovalov theorem was then generalised to apply to multicomponent systems in the thorough work of Sorel and Jouguet. The results of this work have been published in Prigogine and Defay's textbook of fundamental chemical thermodynamics. To the same problem was devoted the more recent work by Storonkin², who was obviously unaware of the work of the French and Belgian investigators".

Firstly, it is untrue that my paper² was "devoted" to the problem of maxima and minima of temperature and pressure, since only a single chapter (14 out of 120 pages) was devoted to this question. Secondly, Korzhinskii is in error in stating that "the problem of temperature and pressure maxima and minima" was considered not only by Konovalov but also by Gibbs only "for binary systems". Indeed, Gibbs gave derivations and formulations of his laws which are correct for any n -component heterogeneous system having a maximum or minimum pressure or temperature. Gibbs (ref. 3, p. 99; ref. 4, pp. 146, 147) showed