OPERATING INSTRUCTIONS

For

RDE 3 POTENTIOSTAT

From

Pine Instrument Co.,
Grove City, Pennsylvania

Including

A BRIEF INTRODUCTION

To The

THEORY AND TESTING

Of

ΓATING DISC AND RING-DISC ELECTRODES

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Introduction

Effective use of the ring-disc electrode requires independent potential control of both the ring and disc electrodes. The RDE 3 has been engineered specifically for ring-disc electrodes. It can also be used with non-rotating electrodes and flow cells.

Warranty

Pine Instrument Company (PIC) warrants all Electro-chemical test equipment it manufactures to be free from defects in materials and workmanship under normal use and service, and agrees to repair or replace any unit (if returned to our plant) which fails to perform properly within six (6) months after date of shipment. This warranty shall not apply to any unit which has been:

1) Repaired, worked on or altered by person(s) unauthorized by PIC;
2) Subject to misuse, negligence or accident;
3) Or connected, installed or used not in accordance with instructions furnished by PIC.

This warranty is in lieu of any other warranty, expressed or implied.

PIC may, at its own discretion, permit a qualifed person not employed by PIC to make minor repairs and adjustments on some equipment, if and only if that person has first contacted the factory and consulted with the repair department at PIC and received instructions and permission from the factory to attempt the repair or adjustment. If such permission is granted by PIC, the unit's warranty shall not be voided by such adjustment or repair attempts.

Initial Inspection

The Potentiostat should be inspected for shipping damage immediately after unpacking. If any damage is found, please notify the carrier and Pine Instrument Company.

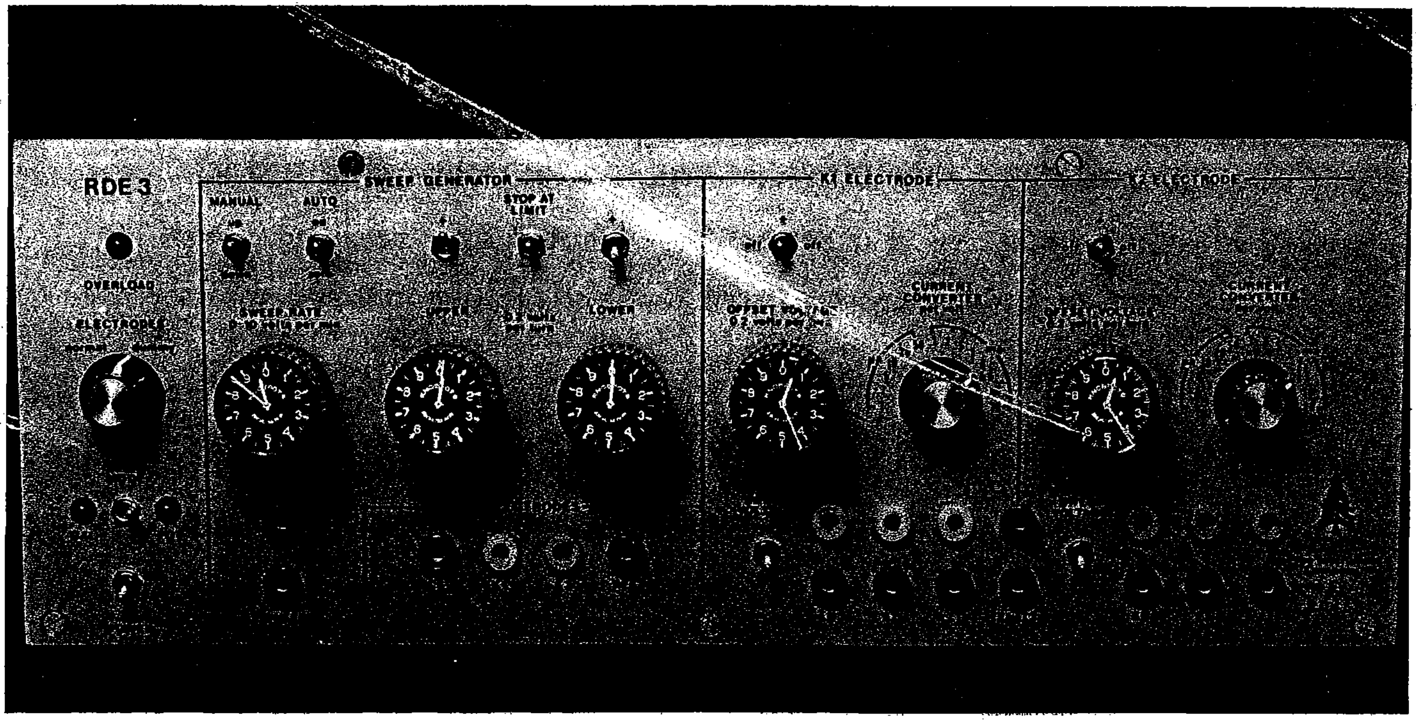

Figure 1. RDE 3 Potentiostat

Features

1. Four electrode potentiostat
2. Can be used as a three electrode potentiostat
3. May be used in galvanostat mode
4. Current-to-voltage converter circuits to give output signal voltages proportional to the electrode currents
5. F.E.T. amplifiers for measuring electrode voltages
6. Set of internal resistors can be switched in place of the external electrodes
7. Outputs protected against short circuits
8. Overload indicator
9. Auxiliary input jacks for applying an external voltage or program to either or both working electrodes
10. Calibrated adjustable offset voltages which can be applied independently to the two working electrodes
11. Summing circuits which will sum all electrode input signal voltages, apply sum to the electrode and provide an output voltage signal for recording
12. Controlled scan sweep generator whose output voltage can be applied to either or both working electrodes
13. Provision to set sweep to stop at a given voltage

General Description

The sweep generator which supplies a sweep or scan signal to the electrodes is ideally suited for this type of operation. Particular attention was given to the design so that an operator will have complete flexibility in adjusting, sweeping, or stopping the sweep at any point in a particular cycle.

This is a true sweep generator in that the period or frequency is not controlled, but rather the rate of sweep and the upper and lower limit of the sweep are the controlled factors. The two limits can be a few millivolts apart or up to four volts apart; these limits can be set both positive, both negative, or one positive and one negative.

In repetitive sweep, the upper and lower limits of sweep are independently adjustable between -2 volts and +2 volts. The output signal sweeps between the high and low limits at the set sweep rate. The sweep can be stopped at any point and held, then started in either direction from the stop point at the discretion of the operator.

In normal operation the sweep generator is free running. If desired, the sweep generator can be set to automatically stop at either end of the sweep. The voltage will hold at that point until the sweep circuit is started again.

The potential control or potentiostat section makes use of the latest circuits and components to give the most versatile and reliable instrumentation while maintaining simplicity of operation. The potential is controlled independent of the current flowing in the cell, and the potential applied to one electrode will not affect the potential or current of the other electrode. The rise time of the amplifiers in the potentiostat is 0.5 volts per microsecond.

A jack is provided which is marked I1-I2. The voltage here is proportional to the difference between the currents flowing in the two electrodes. This will allow measurements where one can subtract out background signals in identical electrodes.

Whenever an overload condition is reached the overload indicator light will come on to indicate a possible error in the measurements. The circuits continue to function even though the indicator is on.

To use the RDE 3 as a 3-electrode potentiostat it is not necessary to make any connections to the K2 electrode circuit.

The K1 or disc electrode can be set on a galvanostat mode. In this situation the signal voltage applied to the K1 input is converted to a current determined by the setting of the current knob.

Noise

The eight black banana jacks on the RDE3 front panel are circuit common, and are floating with respect to the RDE3 case. On some systems it may be necessary to connect one of the black banana jacks to earth ground in order to reduce noise in the system.

The RDE3 is equipped with a three-wire power cord. The RDE3 case is electrically connected to the green wire, or to the normal ground pin on the 115 volt 3-prong plug. The case is therefore connected to earth ground when the RDE3 is plugged into a three-prong outlet with a good quality earth ground connection.

All cables connected to the RDE3 front panel, especially the electrode connections, should be kept as short as possible. Also, it may be necessary to use a shielded wire to connect from the REF electrode jack to the reference electrode. One end of the shield should be connected to any of the black jacks; the other end should be left open. The use of shielded cables on the remaining electrode connections may be desirable.

It is suggested that no connections, other than to the actual electrodes, be made to the ELECTRODE jacks, particularly the REF jack.

Oscillations

The RDE3 is an analog system which relies on feedback for stable operation. There is the possibility, on certain systems, that the feedback may become phase shifted and cause the unit to oscillate. This may manifest itself in various ways to the operator. It is suggested that any time an abnormal situation occurs on the RDE3 - including jumps in potential, or current or the overload indicator glowing for no apparent reason - an oscilloscope be used to observe the outputs.

If oscillations are evident, and the techniques noted in the section on noise do not eliminate the problem, there are four jacks on the back panel to which capacitance may be connected to slow the response of the RDE3. It is suggested that 0.001 - .luf be added to the K1 jacks and/or K2 jacks. Various combinations should be tried, as experience will best dictate what should be used. The capacitors should be either film or ceramic type, 15 volts minimum.

Explanation of Switch Functions

SWITCH FUNCTION	DESCRIPTION
AC Power	Up/On - Down/off
Mode	Right/Potentiostatic Operation Left/Galvanostatic Operation
Electrodes	Normal/Connects electrode Jacks into circuit Dummy/Connects a set of internal resistors into the circuit
	SWEEP GENERATOR
Manual	Up/Sweeps in positive direction Center/Has no effect on sweep output Down/Sweeps in negative direction
Auto	Up/On for automatic sweep operation Center/Sweep holds at the value at time of switching Down/Zero Sweep output is zero
Sweep Rate Pot	A calibrated 10-turn pot for adjusting the sweep rate from 0-10 volts per minute
Upper, Lower Pots & Associated Toggle Switches	The pots are 10 turn calibrated units that give 0.2 volts per turn and set the values of the upper limit and lower limit respectively; used in conjunction with the toggle switch directly above each, the values may be set to either polarity. (Note: The "upper" value must be more positive than the "lower" value.)
Stop at Limit Switch	Left/The unit will sweep to the upper limit and hold. Center/The unit will cycle continuously between the upper and lower limits if auto switch is on. Right/The unit will sweep to the lower limit and hold.

SWITCH FUNCTION	DESCRIPTION
	K1 & K2 ELECTRODE SECTIONS
Offset Voltage Pot & Associated Toggle Switch	The 10 turn pot is calibrated to give 0.2 volts per turn and sets the magnitude of the applied voltage. With the toggle in the center or Off position - no effect on electrode Up Position/Positive polarity on electrode Down/Negative polarity on electrode
Sweep Voltage	Up/On-Output of sweep generator is applied to the electrode Down/Off-No effect on electrode voltage
Current Converter Rotary Switch	Sets the scale factor of converting volts on Jack "I" to actual current in the electrode.

Specifications

Sweep Rate: 0-10 volts per minute

Sweep Range: +2 volts to -2 volts

Electrode Current: 300 milliamp maximum

Electrode Voltage: ±10 volts

Amplifier Response: 0.5 volts per microsecond

Offset Voltage: ±2 volts with calibrated dials

Current Converters: 1 microamp per volt to 20 milliamp per volt in 14 steps

Input Impedance of Reference Potential Follower: 10^{12} ohm

Power: 117 V 50/60 Hz (220 V 50 Hz optional)

Size: 16½" wide x 6" high x 10" deep
42 cm 15.2 cm 25.4 cm

Circuit Description

The first instrument for simultaneous and independent potentiostatic control of the ring and disc electrodes of a rotating ring-disc electrode was described by Napp, Johnson and Bruckenstein (Anal. Chem., 39, 481 (1967)). The circuit of the RDE 3 Potentiostat represents a substantial improvement over the first circuit in terms of capacity, response and convenience. The schematic diagram of the RDE 3 Potentiostat is shown in Figure 3. A brief analysis of the circuit is given here based on the simplified circuit shown in Figure 2.

The circuitry for the potentiostatic control of working electrode 1, K1, consists of the potential follower PF1, the control amplifier CA1, whose output is connected to the counter electrode CE, and the current-to-voltage amplifier C/V. Amplifier C/V maintains the potential of K1 at virtual ground by means of its current feedback loop (R_{F1}). Amplifier CA1 maintains the difference in the potential between electrode K1, E_{K1}, and the reference electrode potential, E_{Ref}, equal to the signal potential, E_1.

$$E_{K1} - E_{Ref} = E_1$$

In practice the potential of K1 is measured directly at the output of PF1.

The circuitry required for potentiostatic control of the second working electrode, K2, consists of the potential follower PF1, the inverter amplifier IA, the control amplifier CA2, and the potential follower PF2. Amplifier CA2 functions by means of its current loop (R_{F2}) to maintain the value of the potential difference between electrode K2, E_{K2}, and the potential of the reference electrode, E_{Ref}, equal to minus the signal potential, E_2.

$$E_{E2} = E_{Ref} = -E_2$$

Hence, the potential of electrode K1 and K2 may be controlled independently of each other. Because the current loop for amplifier CA2 includes electrode K1, it appears at first glance that the independent control of the current through electrode K1 has been destroyed. However, amplifier CA1 operates to maintain the equality $E_1 = E_{K1} - E_{Ref}$ and the counter electrode, CE, serves to complete the current loop for both indicating electrodes. In effect, the current through CE is the algebraic sum of the currents through K1 and K2.

There is an interaction between the two electrode signals in the uncompensated IR drop. Thus, the uncompensated IR drop between the reference electrode and K1 will cause an equivalent loss of potential control in K2. Although this error may be small in many cases, fairly large currents are encountered with convective electrodes, and the uncompensated IR drop must be kept at the lowest possible value by positioning the tip of the reference electrode very close to K1. The potential of K1, as measured at PF1, includes the error resulting from the uncompensated IR drop. When the RDE 3 Potentiostat is used with ring-disc electrodes, K1 is usually the disc electrode and K2 is the ring electrode.

Sweep Generator

The Sweep Generator in the RDE 3 Potentiostat provides the scanning potential signals for cyclic voltammetry at the disc (K1) or the ring (K2) electrodes. The schematic diagram of the Sweep Generator is shown in Figure 3.

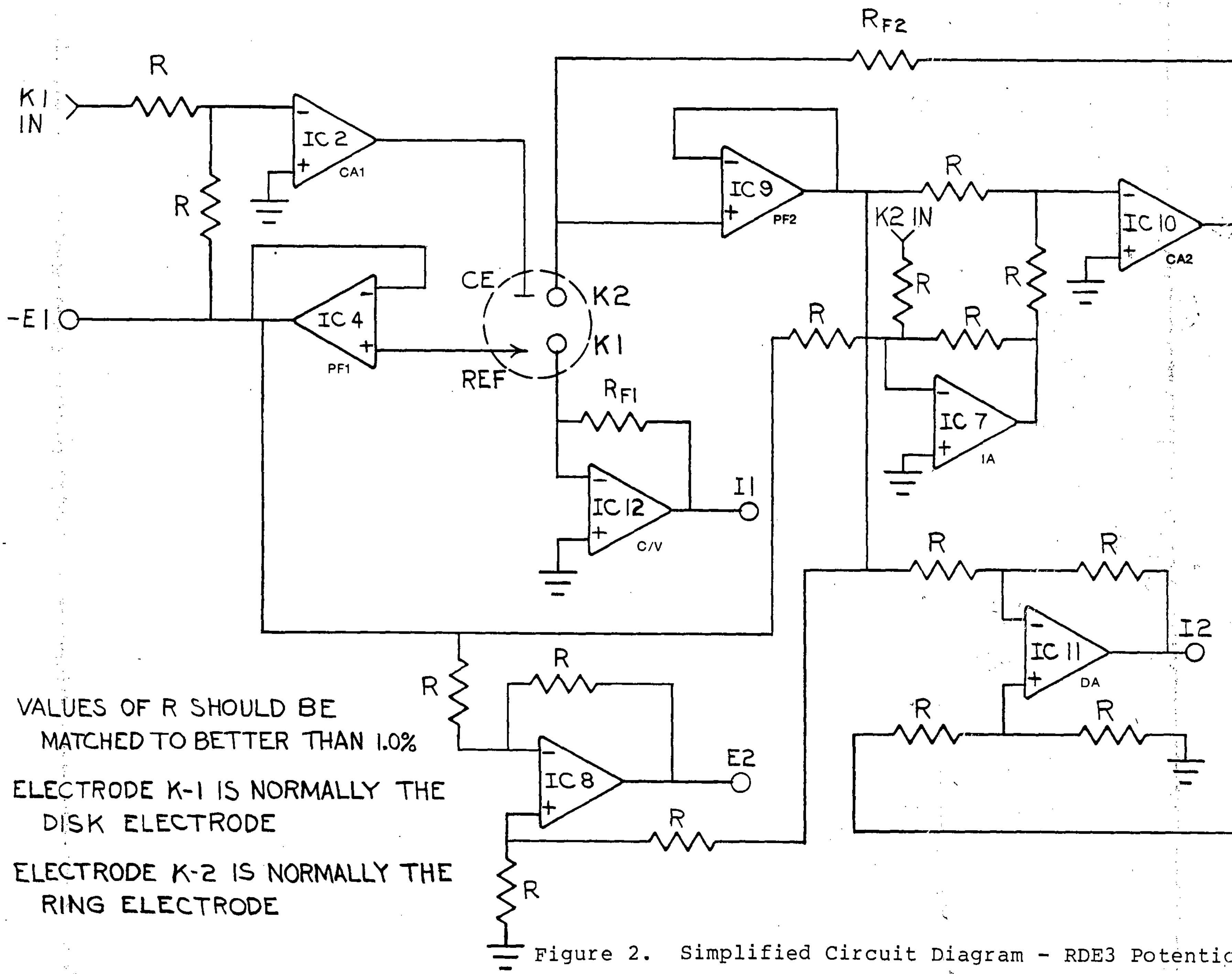

Figure 2. Simplified Circuit Diagram - RDE3 Potentiostat

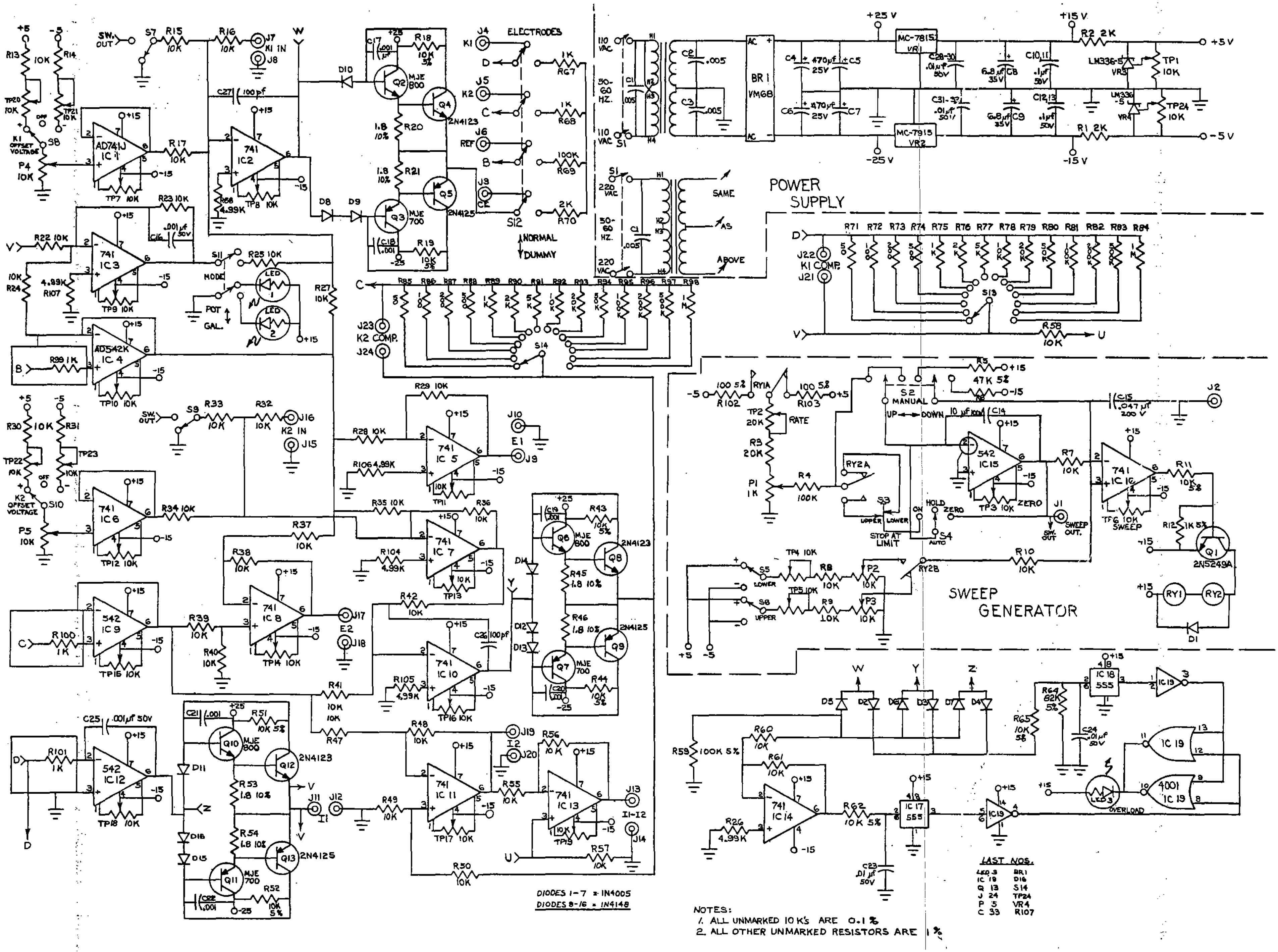

Figure 3. Schematic Diagram - RDE3 Potentiostat

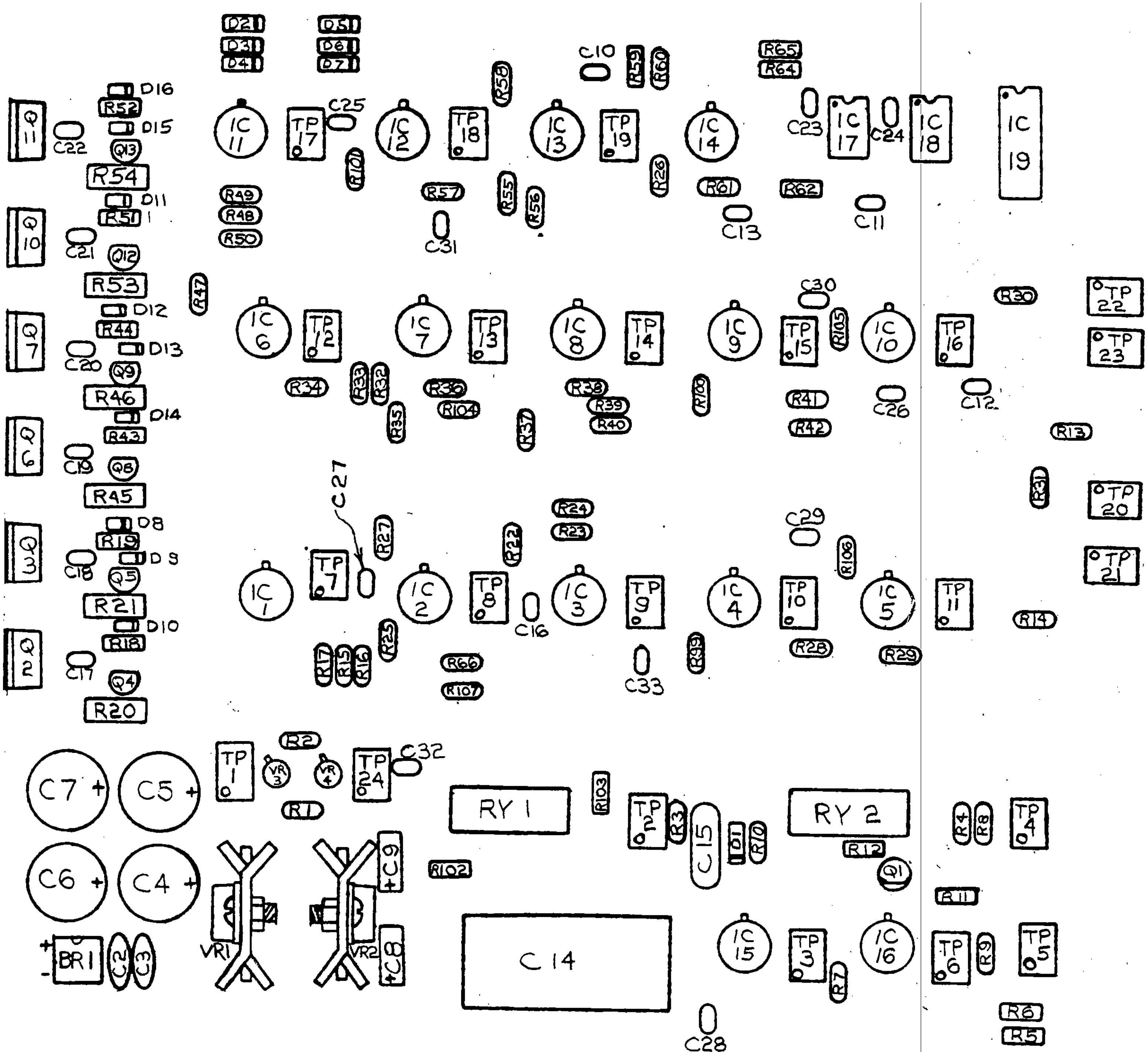

Figure 4: Component Layout - RDE3 Potentiostat

PRELIMINARY TESTING OF POTENTIOSTAT

When a malfunction or some anomalous behavior is observed during electrochemical experiments, one must first determine whether the difficulty originates within the potentiostat or is external to the potentiostat. To facilitate trouble shooting, a so-called dummy cell is located within the potentiostat which is constructed from four resistors with a common connection as shown in Figure 13. When the function switch labelled ELECTRODES at the

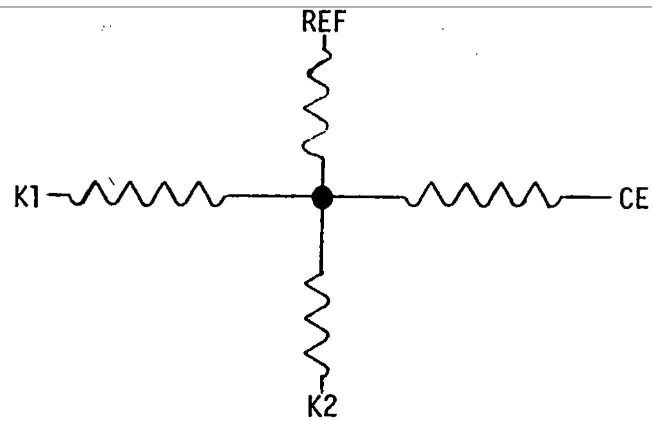

Figure 13. Dummy Cell of RDE 3 Potentiostat

left side of the front panel on the RDE 3 is in the dummy position, all connections to the electrolysis cell are disconnected and internal connections of CE, K1, K2 and REF are made to the dummy cell as shown in Figure 13. In effect, simple resistance analogs are substituted for the functions of the normal electrodes in the electrolysis cell.

Starting with the controls of the RDE 3, and X-Y recorder, set as described in Experiment A, steps 5 and 6, change the ELECTRODES switch from normal to dummy. Change the CURRENT CONVERTER switch on the K1 ELECTRODE section from 0.2 mA/V to 2 mA/V. Turn on the AC POWER switches for the RDE 3, the X-Y recorder and the digital voltmeter (if needed). The recorder pen should be at the ZERO position on both axes and the voltmeter should read 0.00 ± 0.01 V. Commence the potential scan in the positive direction as in Experiment A, step 11. The recorder should display a straight line of slope

+1/2. If the recorder does not display a straight line of slope +1/2, check the leads from the RDE 3 to the recorder; also check all control settings.

Many electrochemical experiments with ring-disc electrodes proceed with potentiostatic control of the ring electrode at a constant potential while the potential of the disc electrode is scanned within certain prescribed limits. Check that the SWEEP VOLTAGE switch for K1 ELECTRODE (disc) is ON and the SWEEP VOLTAGE switch for K2 ELECTRODE (ring) is OFF. Set OFFSET VOLTAGE of K2 ELECTRODE to 0.10 V. The output at the E2 jack should read 0.10 V through the potential scan of the K1 electrode.

Successful completion of the above tests is indicative that the RDE 3 Potentiostat is operating correctly, and that the potentiostat and recorder are properly interconnected. The cause of the malfunction is thus located external to the potentiostat in the connections to the electrolysis cell or within the cell itself. A chart is given below to assist in localizing several commonly encountered problems related to the electrolysis cell. Failure of this test is indicative of a malfunction of the RDE 3 or the X-Y recorder. Consult Pine Instrument Co. for assistance with electronic problems in the RDE 3 Potentiostat.

TROUBLE SHOOTING CHART

Note: The chart below will be of assistance in localizing problems which are commonly encountered in the use of rotating disc and ring-disc electrodes. It is assumed that the dummy cell test described above has been successfully completed.

Problem	Possible Explanation/Suggestions
1. No K1 current recorded over entire potential scan, i.e., Y axis of recorder remains at ZERO; X axis scans normally.	Discontinuity in K1 circuit. Examples: electrode not contacting solution; electrode surface covered with gas bubble; break in lead between K1 jack on RDE 3 and electrode contact on rotator; discontinuity in contact. Suggestion: discontinuities in lead and contact can be checked with ohmmeter.
2. Y axis of recorder is off scale over entire scan, i.e., potentiostat output is saturated.	Reference or counter electrodes not connected to potentiostat. Examples: chambers for counter electrode and/or reference electrode not filled with electrolyte solution; Luggin capillary not filled with electrolyte solution; bubble in Luggin capillary; ground-glass stopcock of Luggin capillary not wetted with electrolyte solution; defective reference electrode. Suggestions: check filling solution of reference electrode; a crystal in the tip of the reference electrode can terminate ionic continuity; replace reference electrode as a temporary test.
3. Electrical noise observed on Y axis of residual current-potential curve, Experiment A, in region of adsorbed hydrogen (0.0 V to -0.2 V <u>vs</u>. SCE).	Dirty electrical contacts on rotator. Suggestion: gently clean contacting surfaces with abrasive paper. Dirty rotator belt resulting in build up of large electrostatic charge. Suggestion: clean belt by soaking in 1:1 HNO_3 for 3-4 hr at room temperature Bubbles impinging on electrode surface during potential scan. Suggestion: N_2 should not be dispersed into electrolyte solution during electrochemical experiments Intermittent discontinuity in leads from RDE 3 to electrolysis cell. Suggestion: Wiggle each lead to determine source System not grounded or ground loops exist between potentiostat and recorder (and voltmeter if used). Pickup of electrostatic noise by reference electrode. Suggestion: when operating the potentiostat at a very high current sensitivity, it may be necessary to place a grounded shield constructed from copper screen around the reference electrode to minimize the pickup of electrostatic noise.

Problem	Possible Explanation/Suggestions
4. Current at E ≈ 0.3 V *vs*. SCE on residual current-potential curve is larger than normal for properly functioning electrode of comparable area at same rotation speed (see Figure 13). In the absence of dissolved O_2, the residual current observed at E ≈ 0.3 V *vs*. SCE on the positive potential sweep is approximately equal in magnitude, but opposite in polarity, to the current for the negative potential sweep. (See Figure 13)	Dissolved O_2 remains in solution. Suggestion: continue deaeration for 10-15 minutes. If proper character of I-E curve is not obtained in region of E ≈ 0.3 V proceed as follows: a. increase rate of N_2 flow; b. improve cell lid to decrease chance of dissolution of air from room atmosphere; Suggestion: use of an unnecessarily long piece of plastic tubing to connect the N_2 tank and the gas dispersion tube of the cell is not advised because of the permeability of plastic by oxygen
5. Current at E ≈ 0.7 V *vs*. SCE on residual current-potential curve is larger than normal. See I-E curve in Figure 17 for ring electrode which has developed a capillary leak.	Probability that the seal surrounding the electrode has developed a capillary leak. Suggestions: replace electrolyte solution with fresh solution to be certain that electroactive impurities are not present in the cell

NOTES:

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