# Development Of A Field-Portable Digital Potentiostat

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Abstract-The use of potentiostats for corrosion rate studies and activation polarization is very crucial because the weight loss method is limited in corrosion studies. However,commercial potentiostats are expensive for most end users. For these reasons, it was desirable to design and build an inexpensive field-portable potentiostat to interface with electrochemical cell.This paper presents theprocedure and design principles of a portable, digital and inexpensive potentiostat, its construction and testing.PROTEUS® software was used in the design of the different components of the potentiostatand simulation of the potentiostat circuit based on considerations of potentiostatic control and an output current of 0.01 to 1A. The potentiostat was tested in a corrosion cell in which a mild steel working electrode (WE) was immersed in 5%NaCl solution. Ag/AgCl reference electrode(RE) was used as well as a Pt counter electrode(CE). An open circuit potential (OCP) of -0.22 V, exchange current density ($i_o$mild steel,Fe/Fe^{2+}) of 1.5 x 10^{-6} A/cm^2, standard potential of mild steel (E^Omildsteel) of − 0.42V and corrosion penetration rate(CPR) at i_o of 9.18 x 10^{-7}cm/hr and Taffel β value of 0.13 V was obtained for mild steel in 5% NaCl solution. The values of OCP,i_o,E^O ,CPR and β were consistent with values obtained from literature.

Index Terms- Design, Construction, Testing,Potentiostat,Taffel curves

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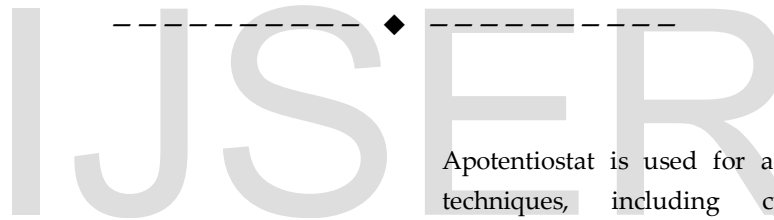
1 Introduction

A potentiostat is an electronic instrument capable of imposing electrical potential waveforms across a working electrode relative to a reference electrode. It also measures the resultant current through the cell at a third electrode. As described by GopinathAshwini and Russell[1], potentiostats are widely used in electroanalytical techniques to identify, quantify, and characterize redox active species including inorganic, organic, and biochemical species. Electroanalytical methods requiring potentiostatic control of the experiment include analysis of corrosion (e.g., Tafel plots), materials properties, and in vivo detection of

Apotentiostat is used for a number of electroanalytical techniques, including cyclic voltammetry (CV). Potentiostats are amplifiers used to control a voltage between two electrodes, a working electrode and a reference electrode, to a constant value. A potentiostat is used for electrochemical characterization of redox active species and in evaluating thermodynamic and kinetic parameters of electron transfer events[2].

In operation, the potentiostat is commonly interfaced to a three-electrode setup. Any electrode combination that meets the fundamental requirements of the electrochemistry being performed could in principlebe used. The reference electrode should approach an ideal non-polarizable condition, examples being Ag/AgCl or calomel electrodes, because this electrode establishes a constant reference potential in the electrochemical cell, against which the working electrode potential may be determined with relatively high precision[3]. This is critical because a change in peak location as small as 1.0 mV can be important in precise electrochemical measurements, for example, when determining thermodynamic or kinetic

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biologicals such as glucose and catechol amines.

parameters for a redox system[4]. While the nature of the reference electrode is important in ensuring the stability of its reference potential, the potentiostat design is also critical. Minimal current is drawn through the reference electrode because its current signal is made input to a large current through the counter electrode such as platinum and various forms of carbon (e.g. glassy carbon, graphite). For a very inexpensive working electrode e.g. lead. (graphite) from a mechanical pencil may be used. In corrosion rate studies, the working electrode is the material being investigated for corrosion.

Current arising from the electron-transfer events at the working electrode is measured at the counter electrode, the reason for which the counter electrode is geometrically larger than the working electrode so that it does not limit the current density at the working electrode. Electron-transfer events at the counter electrode surface are not of interest, and as long as they do not chemically interfere with the analysis, they are ignored. If contaminants would result at the counter electrode, it is placed in a separate compartment from the analyte solution as long as a current pathway is provided between the compartments by, for instance, a salt bridge or sintered-glass frit.

2.0 Methodology

The basic components comprising of a power supply section and the measurement section were coupled on a PROTEUS® software and simulated using power stepped down voltage of 36V from the national grid of 220V to have a variable current output of 0.01A to 1A. The design values of the components were varied on the simulation software until the desired output current was achieved.

2.1 Basic Parts of the potentiostat

Basic parts of thepotentiostat could be grouped into two sections: the measurement section and the power section. The measurement section(Fig.9) comprises of the parts that are linked to the working, reference and counter electrodes (Figs.3-6). The power section comprises of the parts that are linked to bringing in the voltage into the circuitry (Figs.7 and 8).

2.2 Procedures in designing the measurement section

The basic design procedure for the measurement section followed the general principle of potentiostat design (Figures 1 and 2). Electronic potentiostats are generally used for controlling the potential in an electrochemical cell(Fig.1). The potentiostats control the current in the cell from the counter electrode to a working electrode so that the actual potential of the current – carrying working electrode relative to a current – free reference electrode follows a predetermined control voltage and is held constant at its instantaneous value irrespective of electrochemical processes.
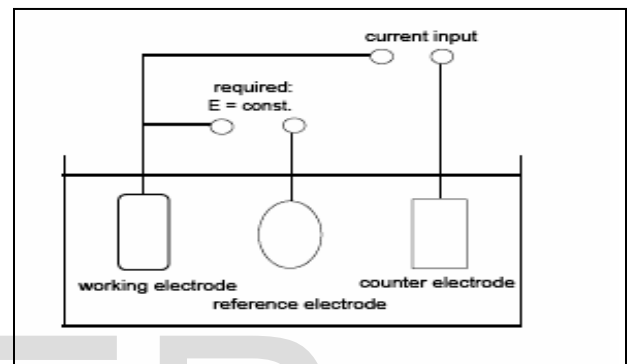

Fig. 1: Principle of a potential - controllable Electrochemical cell [5]

To realize these tasks, an operational amplifier (OPA) 'U' isintroduced(Fig.2) [6] which has two inputs: an inverting input and a non inverting input. When voltage is fed into the non-inverting input, it produces an amplified voltage of same sign. The same voltage fed into the inverting input will give the same amplified magnitude, but of opposite sign. Thus it was imperative to link all the electrodes with OPAs, the working electrode connected to the non-inverting input (+), and the reference electrode to the inverting input (-) and the counter electrode to the output.
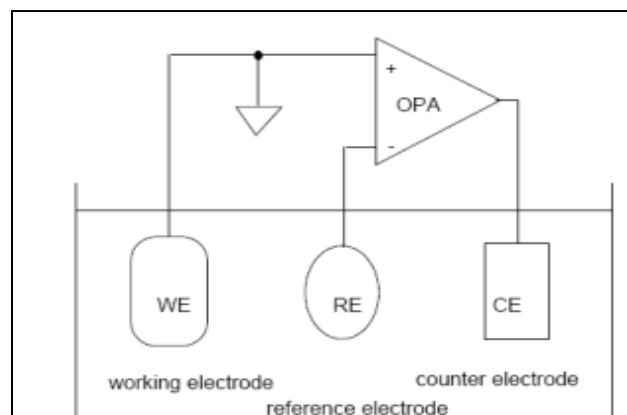
Fig 2: Using Operational Amplifier asPotentiostat[6]

Thus, the difference between the reference electrode and working electrode will be amplified and inverted by the OPA. When a current isfed to the counter electrode CE,the current enters the electrolyte from the counter electrode to the working electrode where a battery cell completes the flow in the circuit. Hence the WE ispolarized so that the difference between the reference electrode and working electrode input is set to zero. This principle was used in the design with UA741 (U1, U2, U3, and U4) operational amplifiers but instead of a battery a 18V and -18V step down voltage from the mains was used.

In other to shift the potential of the WE to some values referring to RE, a voltage was connected in series between electrode input and reference electrode. Since current that flows through the CE is very important to measure, resistor R_1 was connected in the CE wiring across in which voltage can be measured proportional to the current flowing.

Input resistor R_P was connected to protect the RE, which serves to prevent the potential amplifier from being destroyed by static high voltage. A phase capacitor C_1 was also included to stabilize and correct the phase from malfunctioning, due to the variation between the amplifiers relative to frequency.

2.2.1 Amplifiers

Three different types of amplifiers were used: the difference amplifier (Fig.3), the voltage follower amplifier(Fig.4) and the voltage adder amplifier(Fig.5).

2.2.1.1 The difference amplifier

The difference amplifier is needed to obtain the potential difference between two points. An operational amplifier was configured as a difference amplifier for the WE and RE where it was needed to get the difference voltage between the WE and the RE.In the difference amplifier, resistorsR1=R2=R3=R4 (Fig.3), the amplification thus equaling 1. Amplification being equal to 1 implied that the potential difference between A1 and A2 equaled

the potential at B with reference to the ground i.e. $B = \frac{R_3}{R_4}(A_2 - A_1)$.

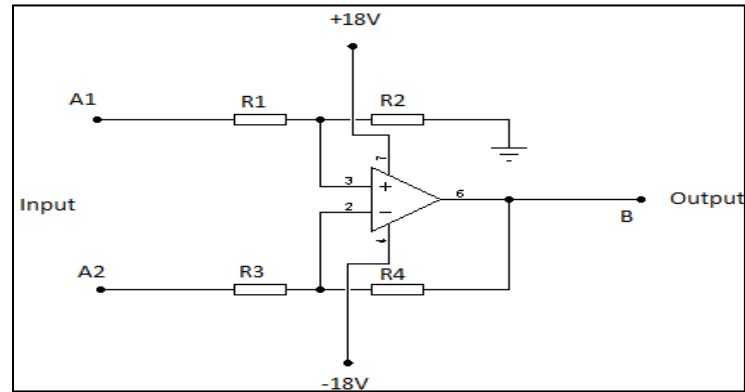To form a differential or balanced output amplifier, it was necessary to take the output feedback.

Fig. 3: The Difference Amplifier with generic resistor values

Another operational amplifier was configured as difference amplifier to measure the potential dropacross a resistor of known resistance (Rm=10kΩ) connected in series between the working electrode and the ground.The current flowing into, or out of the electrolyte could then be determined by applying Ohm's law.

2.2.1.2 Voltage follower amplifier

A voltage follower amplifier is able to supply large current without a noticeable drop in the voltage. This is needed in connection to the CE from where current flows into the electrolyte and hence the WE. A voltage follower configuration was achieved as shown below (Fig.4);
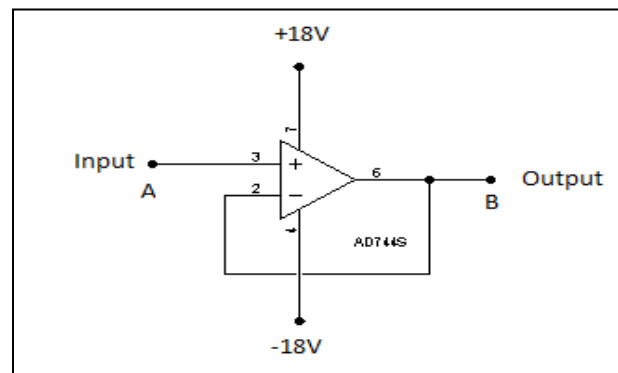

Fig. 4: Voltage Follower Configuration

In this circuit, the voltage at the non-inverting input,A and the voltage at theinverting input approaches the voltage at the non-inverting input and the output,B is at the

samevoltage as the inverting input. Hence, $A(E_1) = B(E_2)$.The introduction of the voltage follower is to increase precision of the measurement section at very low voltages especially if the impedance of the operational amplifier that the voltage source is feeding is high although ideally amplifiers should have zero impedances.

2.2.1.3 Voltage adder amplifier

The voltage adder amplifier (Fig.5),has the ability to add the voltages at the input and amplify the addition to its output, $A_0 = \frac{-R_3}{R_1}(A_1 + A_2 + ...)$.This property is needed in order to vary voltages and consequent current supply to the CE by adding the potential difference between the WE and RE to another variable voltage supply. The amplification was set by making R1=R2=R3. Current in the feedback loop becomes the algebraic sum of the current due to each input. Each source A_1, A_2e.t.c contributes to the total current and no interaction occurs between them.
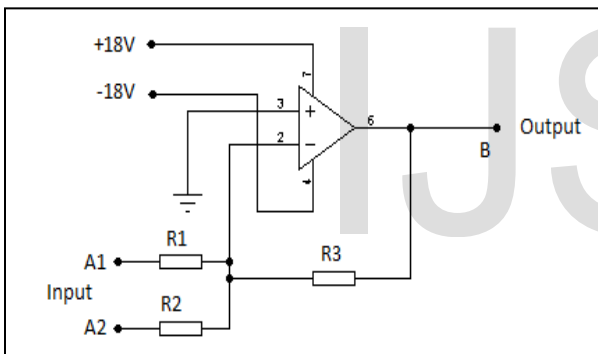

Fig. 5: The Voltage Adder configuration

2.2.1.4 Resistors

These were connected across sections of the circuit to allow passage of electrical current to flow in the electrical circuit. High input resistances of 10KΩ were connected across the circuit to check the amount of current flowing into the OPA to prevent them from static shock.

2.2.1.5 Zener Diode, Capacitor and Variable Resistor

A zener diode, when operated in the breakdown region is known to output a constant voltage. The current flowing through the zener diode is a function of the limiting resistor placed in series with it. In order to prolong the lifespan of the zener diode, we had to limit the current flowing into the

zener diode by connecting a resistor of high resistance10kΩ in series with it. A 1N5242B zener diode, D1 on the main circuit diagram (figure 6) was used and it worked as a 12V constant low power or weak voltage source while R4 limited the current flowing into D1. The capacitor C1 of $10K_F$ helped to improve the stability of the voltage source. Since a variable voltage source is needed, a potentiometer RV1 of 1KΩ was employed to vary the constant weak voltage source.The weak variable voltage source was fed into the operational amplifier configured as voltage follower so as to give us a high power variable voltage source.
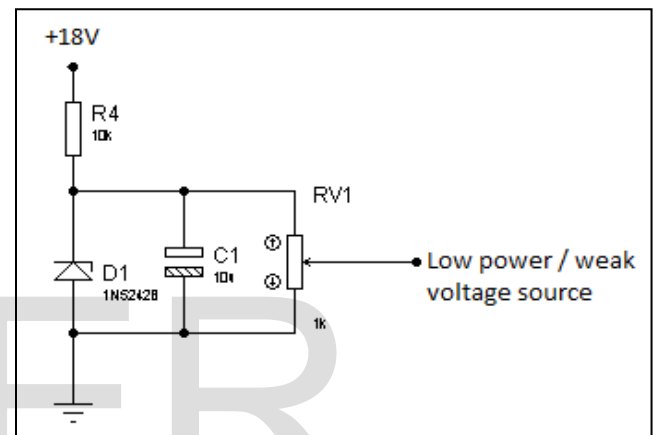

Fig. 6: Circuit Section Linking Zener, Capacitor and Variable Resistor

2.2.1.6 Potential Meters

Two multimeters were used in the circuitry. One for measuring the current flowing as result of the potential drop across a resistor of known resistance (R_M) connected in series between the working electrode and the ground. The second meter for measuring the voltage between the reference electrode and working electrode for the polarization measurement.

2.3   Procedures in designing the power supply section

The power supply consists of a power transformer, junction diodes, fixed resistors and electrolytic capacitors. They are connected together so as to ensure a constant and reliable

power supply needed in the measurement section. The operational amplifier which is the major component in the circuitry was programmed for a +18V, 0V and -18V operation. The power supply section meets this requirement.

A 100W power transformer was selected to convert the 220 volts (AC) supplied by the mains from the national grid to 36 volts (AC). The 36 Volts AC was converted to DC by the help of four junction diodes that areinterconnected to form a bride rectifier BR1 to achieve a full wave rectification(Fig.7). A 2200 microfarad capacitor C2 was then used to filter the output DC voltage of ripples.
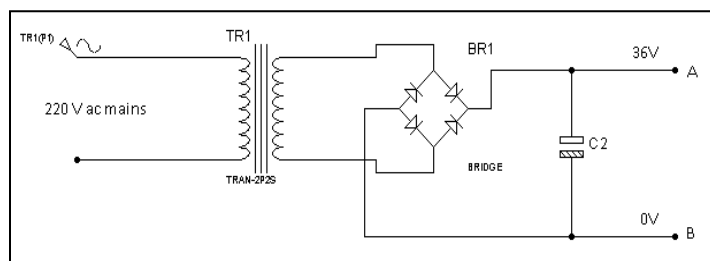

Fig. 7: Complete Power Supply Circuitry

Two fixed resistors were used to divide the 36V DC supply into 18 volts(Fig.8).
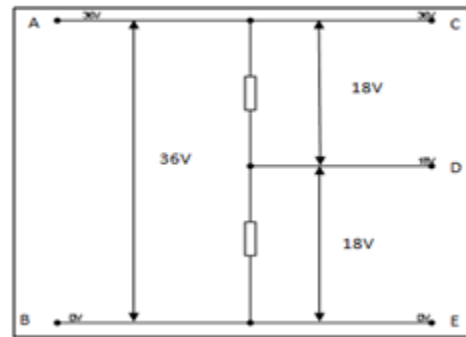

Fig. 8: Achieving +18v and -18v with Fixed Resistors

By grounding point D, it becomes the reference (zero Volt) in the measurement section while points C and E become +18 volts and -18 volts respectively.
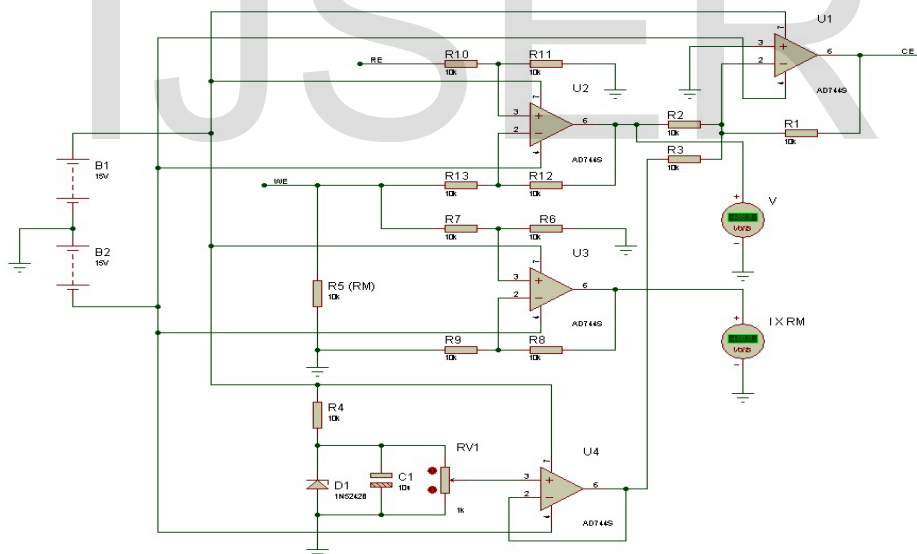

Fig. 9: The schematic of complete potentiostat

2.4 Validation

In this experimentation, the performance of the constructed potentiostat was evaluated in electrochemical media for polarization measurement in 5% NaCl solution.

The potentiostatwas interfaced with three different probes in the electrochemical environment. The probes were Radiometer Copenhagen® Ag/AgCl reference electrode, Radelik® Platinum sheet counter electrode and a mild steel

sample working electrode. These were immersed into 500ml solution of 5% NaCl.

3   Results and Discussion

Figure 10 shows the variation between potential difference (v) and current density (A/cm²) and figure 11 shows the

variation between potential difference (v) and log of current density (A/cm²). The extrapolated lines in figure 10 shows

the theoretical current for the anodic and cathodic reaction whereby the curve lines are the total current which is the sum of the anodic and cathodic currents. Figure 11 shows thestandard potential of mild steel as -0.42 Vcompared with the standard potential of Iron which is -0.44V.

The results from these experiments gave the variation of both potential and current values. The equilibrium potential in the absence of current was taken as Open Circuit Current (OCP), to be

-0.22 V in 5% NaCl environment. This is the corrosion potential in nthe presence of all ions present in solution. This is different from the standard potential for steel.

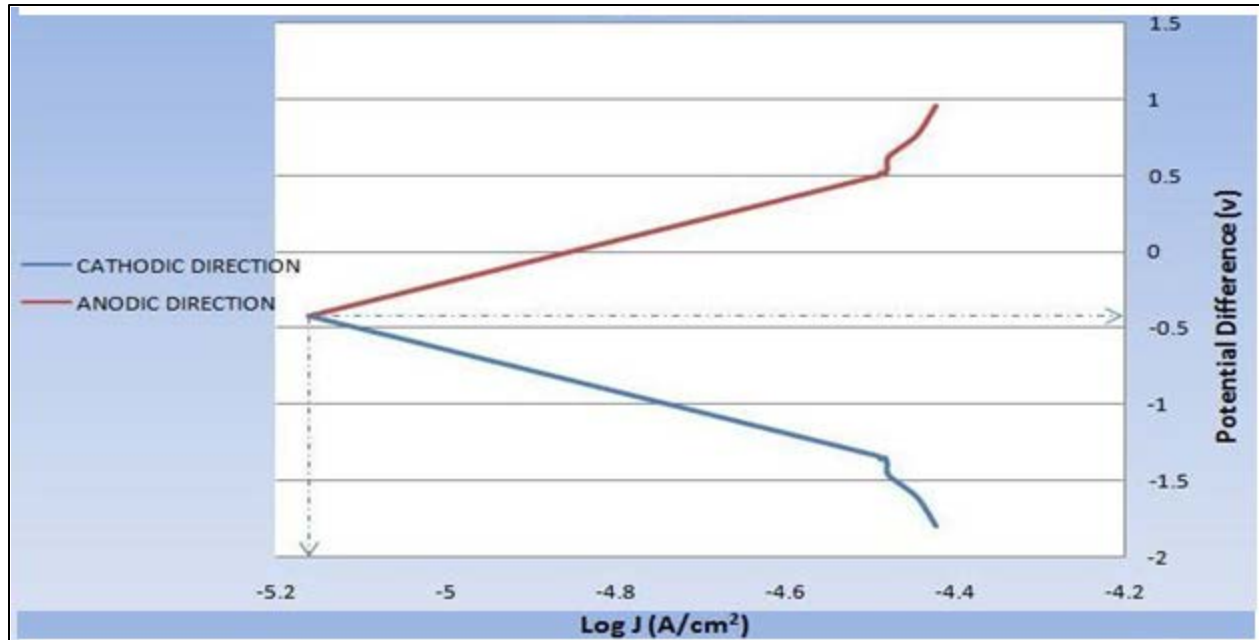Fig. 10: Polarization curves for Mild steel in 5%NaCl solution.

Fig.11: Taffel curves for Mild steel in 5% NaCl solution

Calculation of corrosion rate from the exchange current was:

cpr (rate of decrease of thickness/hr) = $\frac{I_{corr}tM}{n\rho F}$

(vijendra 2005)

where; cpr = corrosion penetration rate in cm/hr,
i_{corr} = the corrosion current in amps/cm^2,
t = equivalent time/hr, m = molecular weight g/mol, ρ = density in grams/cm^3,
f = faraday constant.
 This gave 9.18 x 10-7A/cm^2 being the corrosion rate of mild steel from exchange current density in 5% NaCl solution.

A open circuit potential (OCP) of -0.22 V, exchange current density (i_o mild steel,Fe/Fe^{2+}) of 1.5 x 10^{-6} A/cm^2, standard potential of mild steel (E^O mildsteel) of – 0.42V and corrosion penetration rate(CPR) at i_o of 9.18 x 10^{-7}cm/hr and Taffelβ value of 0.13 V was obtained for mild steel in 5% NaCl solution. The values of OCP, $i_{o,}E^O$, CPR and β were consistent with values obtained from literature [7]. From the literature on galvanized steel corroding in 0.3 to 1MNaCl, it was observed that the corrosion rate were 1.06 x 10^{-7} to 1.16 x 10^{-6}cm/hr [7].

4   Conclusion

This research has achieved the design and construction of simple digitalpotentiostat for corrosion studies. The performance of potentiostat constructed was evaluated for polarization measurement in 5% NaCl. It was observed that the result from the corrosion rate experiment conformed to standard data. Using this validation which has satisfied the aim of this research, it was concluded that the performance of the simple constructed potentiostat gave an excellent agreement with little discrepancy.

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