#### Plasma Cell Waterbath Calorimetry: Data and Analysis (March 11, 2020)

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#### **Summary**

Three calorimetric experiments were observed on March 11, 2020 at BLP, Cranbury. These tests featured the formation and short-time operation of a low-voltage plasma in cylindrical stainless steel cells. The plasma formed between a tungsten electrode and a jet of liquid gallium metal, and was maintained by a DC voltage differential below 40 V. During plasma operation the cells were passively air-cooled in order to achieve high cell temperature. After the plasma was extinguished, the high temperature cell was immersed in a waterbath in order to capture and accurately measure the residual cell thermal energy. The energy flows and enthalpy changes essential to the calorimetric measurement were carefully measured in the tests. These measured quantities were subsequently used with rigorous statements of energy conservation to determine the energy released by the plasma. Here, the plasma energy is defined as energy released in excess of the conventional electrical energy dissipated between the tungsten and liquid gallium electrodes (time integrated voltage-current product). In each test the measured plasma energy was almost three times greater than the input electrode excitation energy. The present document provides a detailed description of the test apparatus, conditions and procedures used in the tests, the development of energy balance formulas applied in the calorimetric evaluation, and analysis of the test data to obtain the plasma energy release.

In each test the main contributors to the calorimetric energy balance were the waterbath sensible heat/enthalpy rise, the bath water vaporization energy, and the electrode input energy. Each of these was measured with high precision and the plasma energy was calculated by difference as indicated in Equation (S1). The bath sensible heat absorption was determined with temperature probes having a differential measurement uncertainty on the order of 0.1%. Further enhancing precision of the water enthalpy rise measurement, vigorous mixing of the bath water resulted in spatial water temperature variations less than 0.01°C when the differential temperature measurement was acquired. Measurement of water vaporization was necessary because the very high temperature plasma cell caused vigorous boiling when immersed in the bath, resulting in considerable water loss and corresponding latent heat loss. Hence, the water mass loss from the bath was measured in each test by a precision balance system which provided a conservative (low) measure of water loss, accurate to within a few percent. The electrode input energy was monitored by high accuracy voltage and current probes at 10 kHz sampling rate to assure adequate resolution of power fluctuations. The cell heat loss by air-cooling prior to immersion in the bath represents a minor but nonnegligible contribution to the energy balance. This loss was estimated from actual cell cooling rates in combination with calculated cell thermal capacitance. Miscellaneous other energy quantities due to various effects such as water agitation/mixing input, hydrogen/oxygen reaction enthalpy, electromagnetic pumping, cell enthalpy change, etc., were all measured in the tests. These, generally minor effects, are grouped in the final term of Equation (S1). It is essential to note that for a non-energetic plasma the terms on the right of (S1) must sum to zero.

Plasma Energy = Bath Sensible Enthalpy Rise + Bath Vaporization Enthalpy - Electrode Energy Input  
+ Cell Heat Loss + 
$$\sum$$
 Miscellaneous Energy (S1)

The measured energy quantities on the right of (S1) are tabulated in Table S1 along with the resultant plasma energy for each of the three tests. In each case the calculated plasma energy release exceeds, in magnitude, each individual energy contribution on the right of (S1). In particular, it exceeds the electrode input energy used to maintain the plasma by at least 20%, and in Test 1 the plasma energy is nearly three times the electrode input energy. Average plasma power was determined from the measured plasma energy and the plasma time duration. The durations were

about 2.95, 13.24, and 3.44 seconds in Test 1, 2, and 3, respectively. The plasma power levels in Table S1 also far exceed the average electrode input power in each test. The energy gain due to plasma energy release is defined as the sum of the plasma and input (electrode) energy, compared to the input:

 $Gain = \frac{Plasma Energy + Input Energy}{Input Energy}$ 

The gain in the three tests ranged from about 220% to 390%, cf. Table S1.

<u> </u>			
	Test 1	Test 2	Test 3
Bath sensible enthalpy rise	284.0 kJ	469.6 kJ	481.9 kJ
Bath vaporization enthalpy	675.9 kJ	342.6 kJ	334.3 kJ
Electrode energy input	274.9 kJ	447.2 kJ	451.9 kJ
Cell heat loss (air-cooling)	167.6 kJ	246.6 kJ	264.5 kJ
$\Sigma$ Miscellaneous energy	-47.3 kJ	-32.0 kJ	-75.4 kJ
Plasma energy release	805.3 kJ	579.6 kJ	553.4 kJ
Plasma power	273.0 kW	43.8 kW	160.9 kW
Plasma energy/Electrode energy	2.93	1.30	1.23
Gain	3.93	2.30	2.23

Table S1. Energy summary: Tests 1-3

## Background

Three calorimetric tests were observed on March 11, 2020 at BLP, Cranbury. These tests were conducted in order to measure the plasma energy release from cylindrical stainless steel reactor cells. The cells were operated in air so that the high cell wall temperature would enhance the plasma reaction and energy release. After a brief time the reaction was extinguished and the cell was immersed in a waterbath so that thermal energy stored in the cells could be captured and accurately measured. This document includes description of the test apparatus and conditions, the development of energy conservation formulas to be applied in the calorimetric measurement, and analysis of the test data to obtain the plasma energy release.

## Plasma cell description

The plasma cell is comprised of a vertical 347 stainless steel tube with 2.88 inch OD, which is partially filled with about 900 g of liquid gallium. The metal is recirculated through a stainless U-tube at the base of the cylindrical chamber by an electromagnetic pump (EMP) as shown in Fig. 1. The upper boundary of the cell is comprised of 4-1/2 inch bored and blank Conflat flanges featuring an isolated feed-through/copper bus bar (one-inch diameter). A half-inch diameter tungsten bus bar joins the lower end of the copper bus bar to a large circular concave tungsten counter electrode (about 3.8 cm diameter). The copper/tungsten bus bar assembly is

shielded by a quartz sheath as shown in Fig. 1. A separate tungsten bus bar, 1 cm diameter, penetrates the lower end of the cell and is immersed in the gallium pool. The interior wall of the cylindrical stainless chamber is shielded in the area of the counter electrode and the gallium pool by a 3.2 mm thick boron nitride (BN) liner. A steady flow of hydrogen (2500 sccm) and oxygen (200 sccm) flows transverse to the cell axis, passing through a 2-3/4 inch Conflat flange. This mixture reacts in the presence of platinum catalyst and flows through the chamber as a mixture of hydrogen and water vapor before being evacuated through a one-inch vacuum port. A steady jet of liquid gallium, driven by the EMP, exits a tungsten nozzle at the end of the U-tube at the base of the chamber and falls back into the gallium pool due to gravity. A steady plasma forms above this jet owing to a small DC voltage which is maintained between the gallium pool, at the potential of the lower bus bar, and the counter electrode. The internal temperature of the cell is measured by two K-type thermocouple probes which are immersed in the liquid gallium, cf. Fig. 1.



Figure 1. Plasma cell schematic diagram

## Calorimetric measurement procedure

The calorimetric measurement of plasma energy was achieved in a two-step process. The plasma reaction was operated first with passive air cooling in order to achieve high cell temperatures which are known to promote greater plasma power output. This first phase of the process lasts only a few seconds in order to avoid cell damage due to extreme plasma temperatures. At the end of this phase, power to the electrodes and the EMP is discontinued along with the  $H_2/O_2$  gas supply, which extinguishes the plasma. The gas supply and exhaust lines and the electrical cables are then promptly disconnected and the cell, still at high temperature due to rather inefficient air-cooling, is quickly re-sealed and immersed in the water bath. Over the next several minutes the large residual thermal energy stored in the cell is released to the bath. This energy is almost completely captured by the bath whose temperature rise is readily measured with two high precision thermistor probes.

The two-step calorimetric process is shown schematically in Fig. 2. Initially, the cell is charged with liquid gallium, sealed, and evacuated to ~40 mTorr pressure. The cell temperature at this time,  $t = t_0$ , is uniform and is denoted by T<sub>Cell0</sub>. Then the 2500/200 sccm hydrogen/oxygen flow is initiated and power is supplied to the electrodes by either the switch-mode rectifier or by discharging a capacitor bank, and the EMP is powered by a current-controlled DC power supply. This results in liquid gallium circulation and plasma formation in the cell chamber, cf. Fig. 1. The robust heat generation causes a rapid rise in cell temperature which requires that the electrode and EMP power, and the  $H_2/O_2$  flow be terminated after only a few seconds, extinguishing the plasma. This time is denoted as t = t'. Subsequently, the power, gas and vacuum connections are disconnected, the cell is sealed and then quickly lowered into the water bath at time  $t = t_1$ . During the air-cooling time interval,  $t_0 \le t < t_1$ , heat is lost from the cell by conduction through the various power and gas connections and by convection and radiation to the laboratory at temperature  $T_{\infty}$ . At the time of immersion t<sub>1</sub> the temperature of the various cell parts, e.g. gallium, cell body, electrodes, flanges, etc., denoted by the running index j = 1, 2, ...,are expected to be non-uniform owing to the strong localized plasma heating prior to power shutdown. While the cell is immersed in the bath, two water jet pumps are operated to enhance convective cooling of the cell and reduce surface boiling, and to ensure bath water temperature uniformity. Because of the high cell temperature when first immersed, vigorous boiling occurs at the surface of the cell. As the vapor bubbles rise toward the water surface, some of the vapor is re-converted to liquid by condensation before escaping from the bath, however, some fraction of the vapor generated reaches the surface and is lost. The water mass lost by vaporization is determined by differential weighing of the bath water, as described below. The cell is allowed to cool in the bath until it reaches approximate thermal equilibrium with the bath water, as indicated by the cell thermocouples and the bath thermistor probes.



Figure 2. Two-step calorimetric process

### Electrode and EMP power supplies, and instrumentation

Electrode power was supplied by a LabView-controlled switch mode rectifier (American CRS Q500 IP32) or by discharging a capacitor bank charged to 48 V. The capacitor bank comprised either four or eight parallel-connected capacitor modules (Maxwell Technologies BMOD0165 P048 C01). Electrode voltage was monitored using a differential probe (PicoTech TA041,  $\pm 70$ V) and current was monitored by a DC Hall effect sensor (GMW CPCO-4000-77-BP10, ±4kA). Electrode voltage and current were sampled by a high-resolution oscilloscope (PicoScope 5000 Series) at 10 kHz sampling rate. Electrode voltage bias was of both possible types: Tungsten counter electrode positive (cathode) and gallium pool negative (anode), or the reverse. The EMP was powered by a programmable DC power supply (Matsusada Precision REK10-1200) in current control mode. The resulting current and voltage supplied to the EMP was very stable and therefore these data were not logged electronically, but rather the mostly constant current and voltage were noted and recorded by hand. The hydrogen (2500 sccm) and oxygen (200 sccm) flows were controlled by separate mass flow controllers (MKS 1179A53CR1BVS for H<sub>2</sub> and MKS M100B12R1BB for O<sub>2</sub>). The bath water jet pumps were a Little Giant 5-MSP (1200 gph at 1 foot head, 125 W) and a much smaller Shysky Tech adjustable speed pump (24 V/50 A, 3600 liter/h). The cell internal temperature was monitored by two 1/8 inch K-type (ungrounded) thermocouple probes, cf. Fig. 1, which extended about one cm into the gallium pool. Cell temperature and bath temperature data were sampled at one second intervals and saved by the data acquisition system.

Water bath temperature is an essential element of the calorimetric measurement, requiring high precision. Bath temperature was measured by a pair of Parr 1168E2 thermistor probes which were immersed into the bath several inches below the water surface on opposite sides, near the bath wall. The probes were monitored via a dual digital thermometer readout (Parr 6775A). Absolute, differential and relative differential accuracy, and resolution and repeatability for the probe/readout system are tabulated in Table 1. Of greatest importance in the present calorimetric measurement is the relative differential accuracy, which is the uncertainty in measuring a one degree C change in temperature. This is less than 0.2% for this probe/readout combination, cf. Table 1, which is more than adequate for accurate measurement of the bath water temperature rise. However, the 0.1°C absolute accuracy (limited by probe interchangeability) suggests that an indicated temperature difference as large as 0.2°C could exist between the two probes when maintained at the same temperature. This is insufficient for accurately evaluating bath spatial temperature uniformity since the rise in bath temperature itself is typically less than 1°C. This difficulty was resolved by a calibration test, performed by BLP, which demonstrated that the two specific probes used for measuring bath temperature differ by no more than ~0.003°C when the two probes are maintained at the same physical temperature. This calibration test is described in Appendix 1.

Absolute accuracy: 10-40°C range	0.1°C
Differential accuracy: 15°C interval	<0.02°C
Relative differential accuracy	<0.13%
Resolution	0.001°C
Repeatability	<0.001°C

Table 1. Parr 1168E2 probe and 6775A readout specifications<sup>1</sup>

## Waterbath mass loss measurement system

The waterbath comprised 126 kg of deionized water in a stainless steel cylindrical tank (22 in. dia. x 36 in. height) located concentrically inside a larger steel tank (27.5 in. dia. x 44 in. height). The annular space between the tanks, nominally about 2.5 inches, was filled with polyurethane insulation to reduce heat loss from the bath water to the surroundings. The water volume (and hence mass) was precisely determined during the bath fill process by a flow meter (Carlton 062JLP) whose accuracy was verified by direct incremental weighing of the water.

It was shown in preliminary experiments that a very significant fraction of the measured plasma energy was due to mass loss from the bath due to boiling at the cell surface. Therefore, the present system was developed by BLP to accurately measure water mass loss due to vaporization and evaporation. The system encompasses the bath described above in addition to an auxiliary steel tank (27.5 in. dia. x 44 in. height). The bath and the auxiliary tank are mounted on a mechanical balance wherein a steel frame measuring 66 in. x 28 in. wide was mounted on a

<sup>&</sup>lt;sup>1</sup> 6775 Digital Thermometer Operating Instruction Manual Parr Instrument Company, June, 2008.

cylindrical shaft fitted with two roller bearings which functioned as a fulcrum. The two tanks were welded in place at opposite ends of the frame and the auxiliary tank was filled with about 200 kg of water as a counterweight. This resulted in approximate balance of the system. A digital scale (MyWeigh i5500: 5500 g capacity; 0.1 g resolution/accuracy) was placed below the end of the balance/frame nearest the auxiliary tank. With the waterbath filled with 126 kg of water only, water was carefully added to the auxiliary tank until the digital scale registered a definite mass imbalance, near 3 kg. This mass imbalance was recorded, with one gram precision, and then the water jet pumps were installed in the waterbath and the calorimetric test run was started. Following the run, the cell and the water jet pumps were removed from the bath. After a quiescent condition was achieved in the two tanks the mass imbalance (indicated by the scale) was again recorded. The post-test imbalance was always greater than the initial imbalance, confirming that water was lost from the waterbath during the test. The increase in mass measured by the scale is not a direct indication of the mass lost from the bath because the lever arm distances for the bath and scale are different. To account for this a calibration constant was developed in separate calibration experiments which correlated the increase in mass registered on the scale to the actual mass lost by the waterbath. The relationship between the mass changes for the bath, the scale, and the auxiliary tank are developed in Appendix 2. There it is shown that the change in scale mass reading must be multiplied by the calibration constant  $\kappa$ = 1.75 (actually a ratio of lever arm lengths) to obtain the actual mass loss from the waterbath. It is also demonstrated in Appendix 2 that ignoring the mass loss from the auxiliary tank during a calorimetric test (this is necessary as there is no way to accurately determine this loss) results in *underestimation* of the mass loss from the waterbath. Uncertainty in the measurement of water mass loss by this system is on the order of a few grams.

### **Energy conservation**

Energy conservation is developed separately for each step of the two-step calorimetric process, Fig. 2. To rigorously account for the energy changes it is necessary to separately consider the plasma cell and the cell support structure because the thermal response of the structure is mostly passive compared to the cell. The cell parts include the cell assembly with flanges, bus bars, electrodes, gallium metal and EMP components. The EMP is considered part of the cell for energy conservation because it is well-coupled to the plasma chamber and there is continuous circulation of liquid gallium between the EMP and the chamber. The support structure includes the stainless plate on which the cell is mounted, the aluminum base plate and the connecting stainless steel standoffs. The thermal capacities of the various cell and structural parts are denoted as

Cell:  $m_j C_{pj}$ , j = 1, 2, ...Structure:  $m_k C_{pk}$ , k = 1, 2, ... and the assumed temperatures of these parts at key times in the two-step calorimetric process are tabulated in Table 2. In Table 2 the temperatures  $T_{Cell0}$  and  $T_{Cell2}$  are the mean temperatures of the two thermocouple probes extending into the gallium pool at times  $t_0$  and  $t_2$ , respectively, whereas the  $T_{j1}$  are the individual temperatures (generally unknown) of the various cell parts at the time of immersion,  $t_1$ . The support structure is assumed to remain at the temperature  $T_{Cell0}$  throughout the air-cooling phase because the structure is not well-coupled (thermally) to the cell, and little time is available for conduction transfer into these parts because the air-cooling period is usually not much greater than a minute in duration. The bath water temperatures  $T_{w1}$  and  $T_{w2}$  are the averages of the two digital thermometer temperatures at times  $t_1$  and  $t_2$ , respectively. And, the structure is assumed to be in thermal equilibrium with the bath water at time  $t_2$ . The large water jet pump immersed in the bath is also assumed to track the bath water temperature.

Table 2. Assumed temperatures<sup>#</sup> for the cell parts, structural parts and bath water

$t = t_0$	$t = t_1$	$t = t_2$
T <sub>Cell0</sub>	$T_{j1}$ j = 1, 2,	T <sub>Cell2</sub>
T <sub>Cell0</sub>	T <sub>Cell0</sub>	T <sub>w2</sub>
	$T_{w1}$	T <sub>w2</sub>
	$t = t_0$ $T_{Cell0}$ $T_{Cell0}$	$\begin{array}{c c} t = t_0 & t = t_1 \\ \hline T_{Cell0} & J_{j=1,2,} \\ \hline T_{Cell0} & T_{Cell0} \\ \hline T_{w1} \end{array}$

 ${}^{\#}T_{Cell0}$  and  $T_{Cell2}$  are the mean temperatures of the two liquid gallium thermocouples at t<sub>0</sub> and t<sub>2</sub>;  $T_{w1}$  and  $T_{w2}$  are the mean temperatures of the two water bath digital thermometers at t<sub>1</sub> and t<sub>2</sub>.

Energy conservation for the cell during the air-cooling phase, from time  $t_0$  to  $t_1$ , requires

$$\underbrace{\mathbf{E}_{\text{Elect}} + \mathbf{E}_{\text{EMP}}}_{\text{Electric energy inflow}} + \underbrace{\mathbf{E}_{\text{Plasma}}}_{\text{Plasma energy}} - \underbrace{\mathbf{Q}_{\text{Lossc}}}_{\text{Cell heat loss}} + \underbrace{\sum_{\text{H2,O2,H2O}}}_{\text{Net enthalpy inflow}} = \underbrace{\sum_{\text{Cell}} m_j \mathbf{C}_{pj} (T_{jl} - T_{\text{Cell0}})}_{\text{Cell enthalpy rise}}$$
(1)

where

$$E_{\text{Elect}} = \int_{t_0}^{t'} P_{\text{Elect}} dt, \quad E_{\text{EMP}} = \int_{t_0}^{t'} P_{\text{EMP}} dt, \quad E_{\text{Plasma}} = \int_{t_0}^{t'} P_{\text{Plasma}} dt, \quad Q_{\text{Lossc}} = \int_{t_0}^{t} \dot{Q}_{\text{Lossc}} dt,$$
$$\sum_{\text{H2,O2,H2O}} H = \int_{t_0}^{t'} \sum_{t_0} (\dot{m}h)_{\text{H2,O2,H2O}} dt$$

The symbols E, P, H and h denote energy, power, enthalpy and specific enthalpy,  $\dot{Q}_{Lossc}$  is the rate of heat loss from the cell, and  $\dot{m}$  represents the mass flow rates of the gases H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. The small rate of enthalpy transfer due to the hydrogen and oxygen gas flow into the system is shown in Appendix 3 to be proportional to the oxygen molar flow rate and the enthalpy of formation for water vapor. For 200 sccm inflow of oxygen the corresponding rate of enthalpy

inflow is about 66 W. Terms corresponding to the support structure do not appear in (1) because the structure temperature is assumed constant during the air-cooling phase, cf. Table 2.

The basis for energy conservation during the water-cooling phase is the deformable, open thermodynamic system which includes the water in the bath as well as the cell and cell support structural parts immersed in it. It was shown in the November, 2019 report on waterbath calorimetry that energy conservation for this system from  $t_1$  to  $t_2$  requires

$$(E_{WJ} - Q_{Lossb}) = \underbrace{[m_{w1}C_{pw} + m_{WJ}C_{pWJ}](T_{w2} - T_{w1}) - \delta m_w h_{vap2}}_{Net bath enthalpy rise due to temperature increase and water vaporization} + \sum_{Structure} m_k C_{pk} (T_{w2} - T_{Cell0})$$

$$(2)$$

where

$$\left(\mathbf{E}_{WJ} - \mathbf{Q}_{Lossb}\right) = \int_{t_1}^{t_2} \left(\mathbf{P}_{WJ} - \dot{\mathbf{Q}}_{Lossb}\right) dt$$

is the net energy added due to water jet pump power and heat loss from the bath, the subscript WJ refers to the water jet pumps,  $\dot{Q}_{Lossb}$  is the rate of heat loss from the bath, and  $\delta m_w$  and  $h_{vap2}$  are the change in bath mass due to vaporization and the water enthalpy of vaporization at bath temperature  $T_{w2}$ .

Adding equations (1) and (2) results in energy conservation for the two-step process overall:

$$E_{\text{Elect}} + E_{\text{EMP}} + E_{\text{Plasma}} - Q_{\text{Lossc}} + \sum_{\text{H2,O2,H2O}} H + (E_{\text{WJ}} - Q_{\text{Lossb}})$$
$$= [m_{w1}C_{pw} + m_{WJ}C_{pWJ}](T_{w2} - T_{w1}) - \delta m_w h_{vap2} + \sum_{\text{Cell}} m_j C_{pj}(T_{\text{Cell2}} - T_{\text{Cell0}}) + \sum_{\text{Structure}} m_k C_{pk}(T_{w2} - T_{\text{Cell0}})$$

Isolating  $E_{Plasma}$  on the left yields the plasma energy release:

$$E_{\text{Plasma}} = [m_{w1}C_{pw} + m_{wJ}C_{pWJ}](T_{w2} - T_{w1}) - (E_{\text{Elect}} + E_{\text{EMP}}) - \delta m_{w}h_{vap2} + \sum_{\text{Cell}} m_{j}C_{pj}(T_{\text{Cell2}} - T_{\text{Cell0}}) + \sum_{\text{Structure}} m_{k}C_{pk}(T_{w2} - T_{\text{Cell0}}) + Q_{\text{Lossc}} - \sum_{\text{H2,O2,H2O}} H - (E_{wJ} - Q_{\text{Lossb}})$$
(3)

Note that the change in water mass  $\delta_{mw} < 0$  so this term represents a positive contribution to the plasma energy, and the mostly unknown temperatures of the various cell parts at the time of immersion,  $T_{j1}$ , do not appear in (3). And further, the form of (3) is such that the enthalpy

changes of the cell and support structure are small relative to the sensible and latent enthalpy changes of the bath water owing to the small overall change in temperature for the cell and structure. This implies that the computed plasma energy generation is insensitive to the thermal capacities of the cell and structure, which may not be known precisely.

#### Water jet and bath heat loss net energy

An estimate of the net energy added to the bath by the water jet pumps and bath heat loss is needed to evaluate the plasma energy, (3). During the water cooling phase the power input to the water jet pumps is mostly constant. And the rate of heat loss from the bath is mostly constant because this is a function of the difference between the bath water temperature  $T_w$  and the environment temperature  $T_{\infty}$ , which changes little owing to the small bath temperature rise. Since these rates are effectively constant the net rate of energy addition to the bath  $P_{WJ} - \dot{Q}_{Lossb}$  can be evaluated from bath energy conservation at any convenient time during the water-cooling process. Near the end of the water cooling phase,  $t \sim t_2$ , the cell temperature is well below 100°C so evaporation losses from the bath are negligible, and the cell is nearly isothermal at the gallium temperature  $T_{Cell2}$ , so energy conservation in rate form simplifies to (compare with Eq. (2))

$$\begin{split} P_{WJ} - \dot{Q}_{Lossb} &= \left[m_{w2}C_{pw} + m_{WJ}C_{pWJ}\right] \left[\frac{dT_{w}}{dt}\right]_{t=t_{2}} + \left(\sum_{Cell} m_{j}C_{pj}\right) \left[\frac{dT_{Cell}}{dt}\right]_{t=t_{2}} + \left(\sum_{Structure} m_{k}C_{pk}\right) \left[\frac{dT_{w}}{dt}\right]_{t=t_{2}} \\ &= \left(m_{w2}C_{pw} + m_{WJ}C_{pWJ} + \sum_{Structure} m_{k}C_{pk}\right) \left[\frac{dT_{w}}{dt}\right]_{t=t_{2}} + \left(\sum_{Cell} m_{j}C_{pj}\right) \left[\frac{dT_{Cell}}{dt}\right]_{t=t_{2}} \end{split}$$

where  $m_{w2} = m_{w1} + \delta m_w$  is the final mass of bath water and the time derivatives of the bath temperature  $T_w$  and the cell temperature  $T_{Cell}$  are evaluated at time  $t_2$ . The net rate  $P_{wJ} - \dot{Q}_{Lossb}$  is found to range between 74 and 338 W in the present tests.

#### Thermal capacities for plasma cell and structure

The masses, heat capacities and thermal capacities for the cell and structural parts are tabulated in Tables 3 and 4 along with the total thermal capacity for each. Also, the water jet pump mass, heat capacity and thermal capacity are 4 kg, 0.43 kJ/kg-K and 1.72 kJ/K, respectively. These capacities are generally less than 1% of the thermal capacity of the 126 kg of water in the bath:  $m_w C_{pw} = 526.7 \text{ kJ/K}$ .

Table 3. Cell thermal capacity

	m <sub>j</sub> [kg]	C <sub>pj</sub> [kJ/kg-K]	m <sub>j</sub> C <sub>pj</sub> [kJ/K]
Upper 4-1/2 in. flange (blank)	1.13	0.48	0.542
Copper bus bar in upper flange	0.37	0.385	0.142
Lower 4-1/2 in. flange (bored)	0.78	0.48	0.374
347 stainless cell body	1.94	0.48	0.931
Upper tungsten bus bar/electrode	0.5	0.132	0.066
BN sleeve for electrode	0	0.8	0
Quartz sleeve for electrode	0.06	0.745	0.045
BN plasma chamber liner	0.1	0.8	0.080
Gallium	0.9	0.371	0.334
Lower tungsten bus bar	0.14	0.132	0.018
Gas inlet 2-3/4 in. flanges (blank plus bored)	0.73	0.48	0.350
EMP pump magnet (Sm/Co)	2.2	0.38	0.836
Stainless EMP pump tube	0.06	0.48	0.029
Totals	8.91		3.749

Table 4. Structure thermal capacity

			m <sub>k</sub> [kg]	C <sub>pk</sub> [kJ/kg-K]	m <sub>k</sub> C <sub>pk</sub> [kJ/K]
Stainless i	mounting	plate	1.31	0.48	0.629
Aluminum	n base plat	e	2.72	0.875	2.380
Stainless s	standoffs		0.6	0.48	0.288
Totals			4.63		3.297

## Cell heat loss rate during air-cooling phase

Heat loss from the cell occurs by conduction through the electrical connection cables (as long as they are connected), and by convection and radiation from the cell surface to the environment:

$$\dot{Q}_{\text{Lossc}} = \dot{Q}_{\text{Loss, Cables}} + \dot{Q}_{\text{Loss, C+R}}$$

The loss rate through the cables is assumed to be 2 kW based on calculations carried out for similarly constructed molten metal cells reported on in December, 2019. The loss rate due convection and radiation is of the form

$$\dot{Q}_{Loss,C+R} = h'A(T_s - T_{\infty})^{5/4} + \varepsilon\sigma A(T_s^4 - T_{\infty}^4)$$
 (4)

where  $T_s$  is an effective mean cell surface temperature. The first term assumes steady loss by natural convection and so this term underestimates the convection loss during the rapid initial cell heat-up. Estimation of the convection coefficient h', also an average over the cell surface, is described in Appendix 4 and the surface emissivity is  $\varepsilon = 0.9$  corresponding to stably oxidized stainless steel. The most important parameter in (4) is the effective cell surface area for heat loss, A. This is estimated by fitting (4) to measurements of  $\dot{Q}_{Loss,C+R}$  made during the present

tests. These measurements used cell temperature vs. time data during the later stages of the time interval  $t' < t < t_1$  during which there is no electrode power supply, EMP power or plasma power generation, and after the electrical cables had been disconnected. Using energy conservation and ignoring differences in temperature between the cell parts during the later part of this cool-down phase yields

$$\dot{Q}_{\text{Loss, C+R}} = -\left(\sum_{\text{Cell}} m_j C_{pj}\right) \frac{dT_{\text{Cell}}}{dt}$$

This procedure resulted in three data pairs:

Test 1: 
$$T_{Cell} = 290^{\circ}C; \quad Q_{Loss, C+R} = 1.425 \text{ kW}$$
  
Test 2:  $T_{Cell} = 450^{\circ}C; \quad \dot{Q}_{Loss, C+R} = 3.972 \text{ kW}$  (5)  
Test 3:  $T_{Cell} = 415^{\circ}C; \quad \dot{Q}_{Loss, C+R} = 2.511 \text{ kW}$ 

These data are shown in the plot of  $\dot{Q}_{Loss, C+R}$  vs.  $(T_s - T_{\infty})$  in Fig. 3. Note that in plotting these data the cell surface temperature must be estimated from the measured interior cell (gallium) temperature. This process assumed steady conduction from the gallium pool through the BN liner and the cell wall, and is also described in Appendix 4. For reference, when the cell interior temperature is 500°C the cell surface temperature is about 487°C. Using the cell temperature instead of the surface temperature overestimates the radiative heat loss by about 7% at this condition. In any case, by fitting (4) to the data (5) results in the effective cell surface area A =  $0.227 \text{ m}^2 = 2270 \text{ cm}^2$ . This is approximately a 19 inch square area.



Figure 3. Cell heat loss due to air-cooling

Because the relation between  $T_s$  and  $T_{Cell}$  is known via the conduction relation (Appendix 4), Eq. (4) can be used to calculate the rate of cell heat loss for each measurement of  $T_{Cell}$  during the aircooling phase of a test. The corresponding energy loss is

$$Q_{\text{Loss, C+R}} = \int_{t_0}^{t_1} \dot{Q}_{\text{Loss, C+R}} (T_{\text{Cell}}) dt \qquad (6)$$

The energy loss due to conduction in the electrical cables is assumed to occur only during the initial half of the time interval between power shutoff and cell immersion in the bath:

$$Q_{\text{Loss, Cables}} = \int_{t'}^{t'+(t_1-t')/2} \dot{Q}_{\text{Loss, Cables}} dt$$
(7)

## Waterbath calorimetry tests

Three tests, performed on March 11, 2020, are analyzed. The cell configuration was the same in each case: 900 g gallium; BN plasma chamber liner;  $2500/200 \text{ sccm H}_2/O_2$  flow. Power to the cell electrodes was supplied by capacitor discharge in Test 1 (four modules) and Test 3 (eight modules), whereas the switch mode rectifier was used in Test 2. One large water jet pump and

one small pump was used for bath mixing in each test. The water mass loss was determined slightly differently in Test 1 compared to the other two tests since, in Test 1, the cell was dry when immersed in the bath. This resulted in the use of a slightly larger drip-loss correction than the other two tests. All data used in the calculation of plasma energy release are tabulated in Appendix 5 for each test.

#### <u>Test 1</u>

In this test power was supplied to the cell electrodes by discharging four capacitor modules over a period of 2.95 s as shown in Fig. 4. Because of the capacitor discharge, current and power generally decayed during this period while voltage was mostly constant at about 30 V. Current decayed from about 5.5 to 2 kA and power reduced from about 180 to 60 kW. Voltage and current fluctuations were small and therefore so were the power fluctuations. Trapezoidal integration of the power during the 2.95 s discharge period resulted in the electrode energy  $E_{Elect}$ = 274.9 kJ. The electrode voltage and current behaviors are more clearly seen in Fig. 5 which shows the relationship between the data sampling rate (10 kHz, or one sample every 0.1 ms) and the voltage and current fluctuations at around 11 s. The smallest time divisions in this plot are 200 microseconds apart. This plot demonstrates that the voltage and current are well behaved and so the 10 kHz sampling frequency is sufficient for accurate measurement of the instantaneous power and electrode energy.



Figure 4. VI data: Test 1



Figure 5. VI data with expanded time scale: Test 1

The cell and bath temperature histories are plotted in Fig. 6 where the time axis is independent of the one used for the electrode power in Fig. 4. This is because data acquisition of the VI and temperature data were not triggered at a common time. It was therefore necessary to estimate the time that electrode power started and the time that cell immersion occurred from temperaturetime gradients in the cell temperatures. Using this approach, electrode power started at time  $t_0 =$ 313 s, at which time the cell temperature is  $T_{Cell0} = 39.67^{\circ}C$ . Power is terminated 2.95 s later at time t' = 315.95 s. The cell temperature rises sharply due to plasma power generation and electrode power input, peaking near 314°C at about 322 s, and then falls rapidly to about 290°C in the next several seconds owing to heat spreading in the cell. Thereafter, cell temperature reduces slowly due to air cooling, until time  $t_1 = 387$  s when immersion begins. The cell power and gas connections are removed during the time interval  $t_1 - t' = 71.1$  s. Before the immersion, t  $< t_1$ , the bath temperature rises slowly owing to power addition to the bath by the water jet pumps, cf. Fig. 6. At time  $t_1 = 387$  s when immersion begins, the cell temperature is approximately 280°C. After this time the cell temperature falls rapidly and the bath temperature rises correspondingly, eventually approaching equilibrium. The test is terminated at time  $t_2 =$ 610 s, about 223 s after immersion. At this time the cell and bath temperatures are 42.86 and 37.549°C, respectively, and the bath temperature rise is 0.539°C. The difference in indicated temperature for the two bath digital thermometers at this time is only about 0.008°C which is less than 2% of the bath temperature rise. This indicates both good bath water temperature uniformity and good precision in the measurement of bath temperature rise.

Immersion of the cell at 280°C results in vaporization loss from bath. The un-calibrated change in the mass scale reading before and after the test was about 273 g. This change was corrected by 70 g for water drip-loss (initially dry cell) and 43 g for evaporation, resulting in a corrected but un-calibrated water loss of 160 g. After calibration this corresponds to about 280 g of actual water loss from the bath. And this, in combination with the enthalpy of vaporization at 37.5°C, 2412.5 kJ [1], corresponds to the removal of 676 kJ of latent heat energy from the bath. The 0.539°C increase in water temperature results in an enthalpy rise of about 284 kJ. The net energy supplied from the water jet pump and bath heat loss is about 53 kJ and the overall enthalpy changes for the cell and support structure are only about 12 and -7 kJ, respectively, because of the small temperature changes of these assemblies. The enthalpy change of the water jet pump is less than 1 kJ.



Figure 6. Cell and bath temperature data plot: Test 1

During the power addition phase, the EMP energy of 0.2 kJ was negligible compared to the 275 kJ supplied to the electrodes. However, the convection and radiation loss from the cell and the conduction loss through the cable connections during the 74 s air-cooling phase are about 97 kJ and 71 kJ, respectively, cf. Eqs. (6) and (7). These result in the overall loss of about 168 kJ from the cell during the air-cooling phase, which is not insignificant compared to  $E_{Elect}$ . The energy addition due to the H<sub>2</sub>/O<sub>2</sub> gas reaction is less than 200 J.

In Test 1 the plasma energy, from Eq. (3), is 805 kJ and the plasma power is 273 kW. That is, the plasma energy release is nearly three times as large as the energy supplied to the cell electrodes,  $E_{Elect} = 275$  kJ. The energy gain due to the plasma in Test 1 is

$$\eta = \frac{E_{Plasma} + E_{Elect}}{E_{Elect}} = \frac{805.3 \text{ kJ} + 274.9 \text{ kJ}}{274.9 \text{ kJ}} = 3.93$$

Key energy data for Test 1 are summarized in Table 5 below and all data used in the energy analysis are tabulated in Appendix 5.

Table 5. Energy summary: Test 1

Plasma energy	805.3 kJ
Plasma power	273.0 kW
Vaporization enthalpy	675.9 kJ
Water enthalpy rise	284.0 kJ
Electrode energy	274.9 kJ
Cell heat loss (air-cooling)	167.6 kJ
Net WJ pump energy/bath loss	52.8 kJ
Gain	3.93

## <u>Test 2</u>

In Test 2 power was supplied to the cell electrodes by the switch mode rectifier over a period of 13.24 s as shown in Fig. 7. This resulted in a mostly uniform voltage level near 25 V but with infrequent, short duration downward fluctuations to near zero voltage. Since the current was mostly constant at about 1.5 kA this resulted in power which averaged between about 35 and 40 kW but with fluctuations which mimicked those in the voltage, cf. Fig. 7. Trapezoidal integration of the power during the 13.24 s period resulted in the electrode energy  $E_{Elect} = 447.2$  kJ. This is thought to be an accurate estimate of the electrode energy since the voltage and power fluctuations are easily resolved by the 10 kHz sampling rate. This is demonstrated, in particular, for the large fluctuation in voltage and power just prior to 16 s in the plots with expanded time scale, Fig. 8. Figure 8 shows that this particular fluctuation occurs over a time interval of about 1.6 ms during which 15 samples of voltage and current are acquired.



Figure 7. VI data: Test 2



Figure 8. VI data with expanded time scale: Test 2

The cell and bath temperature histories for Test 2 are plotted in Fig. 9. In this test electrode power started at time  $t_0 = 127$  s when the cell temperature is  $T_{Cell0} = 40.05^{\circ}C$ . Power is

terminated 13.24 s later at t' = 140.24 s. The cell temperature rises at a rate similar to Test 1, however, the longer duration of the plasma and electrode power results, ultimately, in considerably greater cell temperature. Cell temperature peaks near 571°C at around 143 s, then falls rapidly as heat spreads within the cell. This is followed by more gradual temperature decay due to air-cooling until time  $t_1 = 188$  s when the cell is immersed in the bath. At the time of immersion the cell temperature rises, eventually approaching equilibrium. The test is terminated at time  $t_2 = 430$  s, 242 s after immersion. The cell and bath temperatures at this time are 40.59 and 35.588°C, respectively, and the bath temperature rise is 0.892°C. The difference in indicated temperature for the two bath digital thermometers at this time is only 0.001°C which is only about 0.1% of the bath temperature rise, indicating excellent bath water temperature uniformity and high precision in the measurement of bath temperature rise.

In Test 2 about 142 g of water mass is lost from bath, which is about half as much as the 280 g lost in Test 1. This is unexpected since the cell temperature when immersed was much greater in Test 2: 430°C vs. 280°C. Perhaps the difference is a consequence of lower excess (in excess of the saturation temperature) surface temperature resulting in more effective nucleate boiling in Test 1, as opposed to very high excess surface temperature and film boiling in Test 2. The difference in vapor generation could also be due to more effective aiming of the water jet pump stream at the hottest portions of the cell in Test 2, hence reducing boiling on the cell surface. In any case, the loss of 142 g corresponds to about 343 kJ of latent enthalpy in Test 2. And the water temperature rise of 0.892°C corresponds to about 470 kJ of sensible enthalpy change. Note that the sensible heat absorbed by the bath is much greater than the latent heat loss, which is opposite to the trend in Test 1.



Figure 9. Cell and bath temperature data plot: Test 2

The convection and radiation loss from the cell and the conduction loss through the cable connections in Test 2 are about 199 kJ and 48 kJ, respectively, resulting in the overall loss of 247 kJ from the cell during air-cooling. This is consistent with the lower loss (168 kJ) in Test 1, presumably owing to the considerably lower cell temperature in that test.

The plasma energy and power in Test 2 are about 580 kJ and 44 kW, respectively, and the gain is

$$\eta = \frac{E_{Plasma} + E_{Elect}}{E_{Elect}} = \frac{579.6 \text{ kJ} + 447.2 \text{ kJ}}{447.2 \text{ kJ}} = 2.30$$

Key energy data for Test 2 are summarized in Table 6 below and all data used in the energy analysis are tabulated in Appendix 5.

Table 6. Energy summary: Test 2

Plasma energy	579.6 kJ
Plasma power	43.8 kW
Vaporization enthalpy	342.6 kJ
Water enthalpy rise	469.6 kJ
Electrode energy	447.2 kJ
Cell heat loss (air-cooling)	246.6 kJ
Net WJ pump energy/bath loss	18.0 kJ
Gain	2.30

#### <u>Test 3</u>

In Test 3 power was supplied to the cell electrodes by discharging eight capacitor modules (in contrast to four modules in Test 1) over a period of 3.44 s as shown in Fig. 10. The voltage variation was mostly smooth but voltage decayed gradually from about 35 down to ~25 V during the power addition phase. Current variation was greater than in Test 1, ranging from about 6 kA down to below 3 kA and then rising back to about 5 kA. The current also exhibited greater fluctuations, which are also evident in the electrode power, cf. Fig. 10. Power reached about 200 kW early in the process, decayed to around 115 kW, and then stabilized near 130 kW for the rest of the process. Trapezoidal integration of the power during the 3.44 s period resulted in the electrode energy  $E_{Elect} = 451.9$  kJ, which is considerably more than the 275 kJ in Test 1 (four modules). The fluctuations in the electrode power near 11.2 s in Fig. 10 are better resolved using the expanded time scale in Fig. 11. This figure confirms that the power fluctuations are adequately tracked by the 10 kHz sampling rate, and electrode power and energy are accurately measured.



Figure 10. VI data: Test 3



Figure 11. VI data with expanded time scale: Test 3

The cell and bath temperature histories for Test 3 are plotted in Fig. 12. Electrode power began at time  $t_0 = 543$  s when the cell temperature was  $T_{Cell0} = 37.49$ °C. Power is terminated 3.44 s later at t' = 546.44 s. The cell temperature rise is considerably greater in Test 3 than Test 1 owing mostly to the greater capacitor discharge energy (452 vs. 275 kJ). Cell temperature peaks near 481°C at around 549 s, falls rapidly, and then more gradually as cell temperature decays due to air-cooling. At time  $t_1 = 612$  s the cell is immersed in the bath. At the time of immersion the cell temperature rises, as expected. The test is terminated at time  $t_2 = 840$  s, 228 s after immersion. At time  $t_2$  the cell and bath temperatures are 39.67 and 35.253°C, respectively, and the bath temperature rise is 0.915°C. The difference in indicated temperature for the two bath digital thermometers at this time is again only 0.001°C, indicating excellent bath water temperature uniformity and high precision in the measurement of bath temperature rise.

In Test 3 about 138 g of water mass is lost from bath, which is similar to Test 2 (142 g). The loss of 138 g corresponds to about 334 kJ of latent enthalpy and the water temperature rise of 0.915°C corresponds to about 482 kJ of sensible enthalpy change in Test 3.

![](_page_21_Figure_2.jpeg)

Figure 12. Cell and bath temperature data plot: Test 3

The convection and radiation loss from the cell and the conduction loss through the cable connections in Test 3 are about 199 kJ and 66 kJ, respectively, resulting in the overall loss of 264 kJ from the cell during air-cooling. This is slightly greater than in Test 2 in which the cell temperature was larger, however, the air-cooling time  $t_1 - t_0$  was greater in Test 3.

The plasma energy and power in Test 3 are about 553 kJ and 161 kW, respectively, and the gain is

$$\eta = \frac{E_{Plasma} + E_{Elect}}{E_{Elect}} = \frac{553.4 \text{ kJ} + 451.9 \text{ kJ}}{451.9 \text{ kJ}} = 2.23$$

Key energy data for Test 3 are summarized in Table 7 below and all data used in the energy analysis are tabulated in Appendix 5.

Table 7. Energy summary: Test 3

Plasma energy	553.4 kJ
Plasma power	160.9 kW
Vaporization enthalpy	334.3 kJ
Water enthalpy rise	481.9 kJ
Electrode energy	451.9 kJ
Cell heat loss (air-cooling)	264.5 kJ
Net WJ pump energy/bath loss	77.0 kJ
Gain	2.23

## **References**

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Appendix 1. Bath thermistor probe calibration check: 1168E2 probe/6775A readout

Because the standard absolute accuracy of 0.1°C (limited by thermistor probe interchangeability) implies that differences in indicated temperature for the two probes may be as large as 0.2°C, spurious indications of bath temperature non-uniformity may result. Therefore, BLP carried out a simple calibration check on the two probes used for measuring bath temperature. The two probes, denoted as Probe 1 and Probe 2, were immersed in room temperature water inside an insulated dewar as shown in Fig. A1.1. The probe tips were thermally shorted, as much as possible, by tightly wrapping adhesive tape around the probe shafts, forcing physical contact between the probe tips. The probes were connected to Channel 1 and Channel 2 of the Parr 6775A readout as shown.

![](_page_23_Figure_0.jpeg)

Figure A1.1. Configuration used in probe calibration

In this configuration each probe indicated small fluctuations in temperature, however, the difference in temperature was relatively constant at 0.003°C:

$$T_{Pr1/Ch1} - T_{Pr2/Ch2} \approx 0.003^{\circ}C$$

Here  $T_{Pr1/Ch1}$  is the indicated temperature for Probe 1 read through Channel 1 and  $T_{Pr2/Ch2}$  is the indicated temperature for Probe 2 read through Channel 2. Without disturbing the probe configuration in the dewar, the connections to the readout were switched: Probe 1 was connected to Channel 2 and Probe 2 was connected to Channel 1. Small fluctuations in each indicated probe temperature were again observed and the difference in the indicated temperatures was again relatively constant. The magnitude of the difference was the same as before but the sign was changed:

$$T_{Pr1/Ch2} - T_{Pr2/Ch1} \approx -0.003^{\circ}C$$

The difference in indicated temperature for the probes cannot be deduced directly from these two measurements because it is not certain that the probes are actually at the same temperature. However, assume that the temperature indicated by each probe is the actual probe temperature plus distinct deviations due to an imperfect probe R-T characteristic and due to the particular readout channel used. For example,  $T_{Pr1/Ch1} = T_{1act} + \delta T_{Pr1} + \delta T_{Ch1}$ . Then, the two cases above are

$$T_{Pr1/Ch1} - T_{Pr2/Ch2} = (T_{1act} - T_{2act}) + (\delta T_{Pr1} - \delta T_{Pr2}) + (\delta T_{Ch1} - \delta T_{Ch2})$$
  

$$T_{Pr1/Ch2} - T_{Pr2/Ch1} = (T_{1act} - T_{2act}) + (\delta T_{Pr1} - \delta T_{Pr2}) + (\delta T_{Ch2} - \delta T_{Ch1})$$
(A1.1)

Adding these results in

$$0 = (T_{lact} - T_{2act}) + (\delta T_{Pr1} - \delta T_{Pr2})$$

It is unlikely that the difference in actual probe temperatures is finite and exactly balanced by the difference in the deviations for the two probe R-T characteristics. A more logical conclusion is that the actual probe temperatures are equal (to within less than half a thousandth of a degree) and the deviations in the R-T characteristics are either the same or both zero. Then it follows from either of (A1.1) that the indicated temperatures of the two probes deviate by about 0.003°C when maintained at the same temperature, and this deviation results from unequal deviations in the two readout channels. This small difference in indicated temperature is more than sufficient for evaluating spatial variations in bath temperature.

#### Appendix 2. Water mass loss calculation from balance system

The balance system is sketched in Fig. A2.1 where the lever-arm distances from the balance point to the center of mass of the bath and auxiliary tanks are shown. The force due to the scale,  $f_{scale}$ , acts at a distance  $l_{scale}$  from the balance point and the corresponding mass indicated on the scale is  $m_{scale} = f_{scale}/g$ .

![](_page_24_Figure_5.jpeg)

Figure A2.1. Schematic diagram of balance system

If the system is balanced initially and then the masses of the bath and auxiliary tank change, the scale reading must change to satisfy force-moment equilibrium about the balance point:

Initial: 
$$m_{bath}gl_{bath} + m_{scale}gl_{scale} = m_{aux}gl_{aux}$$
  
Final:  $m'_{bath}gl_{bath} + m'_{scale}gl_{scale} = m'_{aux}gl_{aux}$ 

Subtracting these and denoting the mass changes as  $\delta m_{()} = m'_{()} - m_{()}$  results in the change in mass of the bath

$$\delta m_{\text{bath}} = \delta m_{\text{aux}} \frac{l_{\text{aux}}}{l_{\text{bath}}} - \delta m_{\text{scale}} \frac{l_{\text{scale}}}{l_{\text{bath}}}$$

During a calibration of the balance system, water mass increments  $\delta m_{bathi}$  are removed from the bath in succession and the corresponding changes in scale reading  $\delta m_{scalei}$  are recorded. Because the bath mass increments are relatively large and because each calibration data point is collected over a short time span, the change in mass of the auxiliary tank due to evaporation is negligible during the calibration. Then, during calibration

$$\delta m_{bath} = -\kappa \delta m_{scale}, \quad \kappa = \frac{l_{scale}}{l_{bath}}$$

The calibration factor  $\kappa$ , which yields the mass removed from the bath for a measured increase in scale reading, is simply the ratio of the scale and bath lever arms. Denoting the mass changes during each step of the calibration by  $\delta m_{bath1}$ ,  $\delta m_{bath2}$ , ... and  $\delta m_{scale1}$ ,  $\delta m_{scale2}$ , ... and adding after n mass increments results in

$$\begin{split} \sum_{i=1}^{n} \delta m_{bathi} &= -\kappa \sum_{i=1}^{n} \delta m_{scalei} \\ m_{bath} - m_{bath0} &= -\kappa (m_{scale} - m_{scale0}) \\ m_{bath} &= -\kappa m_{scale} + \kappa m_{scale0} + m_{bath0} \end{split}$$

where  $m_{bath}$  and  $m_{scale}$  are the mass of the bath and the scale reading after n steps. The calibration factor is just the negative slope of the calibration data when plotted as  $m_{bath}$  vs.  $m_{scale}$ , as in Fig. A2.2. The data scatter around the trend line fit in Fig. A2.2 is very low: Maximum deviation = 2.5 g; RMS deviation = 0.95 g. Hence the calibration factor,  $\kappa = 1.750$ , is determined with very high precision.

![](_page_26_Figure_0.jpeg)

Figure A2.2. Calibration data and fitted trend line

During a calorimetric test the change in mass of the bath, including the small change in mass of the auxiliary tank, is

$$\delta m_{\text{bath}} = \delta m_{\text{aux}} \frac{l_{\text{aux}}}{l_{\text{bath}}} - \kappa \delta m_{\text{scale}}$$

Since the mass of the auxiliary tank may decrease but can never increase during the course of a test

$$\delta m_{bath} \leq -\kappa \delta m_{scale}$$

That is, the actual waterbath mass decrease is greater than or equal to the decrease calculated by ignoring the mass loss from the auxiliary tank.

Appendix 3. Enthalpy transfer due to H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O gas flow

Hydrogen and oxygen flows are mixed upstream of the cell. The hydrogen and oxygen react, in the presence of the catalyst, to form  $H_2O$ . Because there is excess hydrogen in the mixture the production of  $H_2O$  is limited by the oxygen flow rate. After reaction, the resulting mixture of hydrogen and water are removed from the cell at low pressure by a vacuum pump. It is assumed that the exiting mixture consists of water vapor and molecular hydrogen and that the gas temperature at the bath inlet and exit are the same. The net enthalpy transfer into the cell due to hydrogen and oxygen inflow is

$$\sum_{\rm H2,O2,H2O} H = \int_{t_0}^{t'} [\Sigma(\dot{m}h)]_{\rm H2,O2,H2O} dt$$

where m denotes mass flow rate. In expanded form the integrand is

$$\begin{split} \left[ \Sigma(\dot{m}h) \right]_{\rm H2,O2,H2O} &= \dot{m}_{\rm H2i} h_{\rm H2} + \dot{m}_{\rm O2i} h_{\rm O2} - \dot{m}_{\rm H2e} h_{\rm H2} - \dot{m}_{\rm H2Oe} h_{\rm H2O} \\ &= \dot{n}_{\rm H2i} \overline{h}_{\rm H2} + \dot{n}_{\rm O2i} \overline{h}_{\rm O2} - \dot{n}_{\rm H2e} \overline{h}_{\rm H2} - \dot{n}_{\rm H2Oe} \overline{h}_{\rm H2O} \end{split}$$

where the subscripts i and e denote inlet and exit,  $\dot{n}$  is molar flow rate and  $\bar{h}$  denotes molar enthalpy. From the reaction stoichiometry the exiting molar flow rates of H<sub>2</sub>O and H<sub>2</sub> are

$$\dot{n}_{H2Oe} = 2\dot{n}_{O2i}, \quad \dot{n}_{H2e} = \dot{n}_{H2i} - \dot{n}_{H2Oe} = \dot{n}_{H2i} - 2\dot{n}_{O2i}$$

Substitution yields

$$\begin{split} \left[ \Sigma(\dot{m}h) \right]_{\rm H2,O2,H2O} &= \dot{n}_{\rm O2i} \overline{h}_{\rm O2} + 2\dot{n}_{\rm O2i} \overline{h}_{\rm H2} - 2\dot{n}_{\rm O2i} \overline{h}_{\rm H2O} \\ &= 2\dot{n}_{\rm O2i} \left\{ \frac{1}{2} \overline{h}_{\rm O2} + \overline{h}_{\rm H2} - \overline{h}_{\rm H2O} \right\} \\ &= -\dot{n}_{\rm H2Oe} \underbrace{\left\{ \overline{h}_{\rm H2O} - \frac{1}{2} \overline{h}_{\rm O2} - \overline{h}_{\rm H2} \right\}}_{-241,826 \text{ J/mol}} \end{split}$$

where the small difference in the enthalpy of formation between the standard state temperature, 25°C, and the cell temperature has been ignored. For a 200 sccm oxygen inflow:

$$\dot{n}_{O2i} = 200 \frac{\text{scc } O_2}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ mol } O_2}{24,400 \text{ scc } O_2} = 1.37 \times 10^{-4} \text{ mol } O_2/\text{s}$$
$$\dot{n}_{H2Oe} = 2\dot{n}_{O2i} = 2.73 \times 10^{-4} \text{ mol } H_2\text{O/s}$$
$$\left[\Sigma(\dot{\text{mh}})\right]_{H2,O2,H2O} = -2.73 \times 10^{-4} \text{ mol } H_2\text{O/s} \times (-241,826 \text{ J/mol } H_2\text{O}) = 66.1 \text{ W}$$

In this case the net rate of enthalpy flow into the cell due to the hydrogen and oxygen inflow is 66.1 W.

<u>Appendix 4.</u> Estimate of cell heat loss rate (air-cooling)

The rate of heat loss from the cell while air-cooling is due to natural convection and radiation from the cell surface at temperature  $T_s$  to the surroundings at temperature  $T_{\infty}$ :

$$\dot{Q}_{\text{Loss, C+R}} = h'A(T_s - T_{\infty})^{5/4} + \varepsilon \sigma A(T_s^4 - T_{\infty}^4)$$
 (A4.1)

In (A4.1) steady convection is assumed, which underestimates the convection loss during the rapid heat-up phase. The convection coefficient h' is estimated from standard natural convection correlations [2] as

$$h' = \frac{0.46k}{L} \left(\frac{g\beta' L^3}{\nu\alpha}\right)^{1/4} \sim 1.5 \text{ W/m}^2 \text{-} \text{K}^{5/4}$$
 (A4.2)

where the air properties have been evaluated at the film temperature and the characteristic length is L = 200 cm. In (A4.1) the surface emissivity is  $\varepsilon = 0.9$  corresponding to stably oxidized stainless steel. The cell surface temperature T<sub>s</sub> is not measured in the tests and is therefore unknown, however, it can be estimated from the measured internal cell temperature T<sub>cell</sub> by assuming steady conduction through the liquid gallium (thickness  $\delta_{Ga}$ ), the BN liner (thickness  $\delta_{Lin}$ ) and the stainless cell wall (thickness  $\delta_{Wall}$ ):

$$T_{cell} - T_{s} = \beta \left( \frac{\delta_{Wall}}{k_{Wall}} \right) \left( \frac{\dot{Q}_{Loss, C+R}}{A} \right), \qquad \beta = 1 + \frac{k_{Wall}}{k_{Ga}} \frac{\delta_{Ga}}{\delta_{Wall}} + \frac{k_{Wall}}{k_{Lin}} \frac{\delta_{Lin}}{\delta_{Wall}}$$
(A4.3)

In (A4.3) the conductivity and thickness data in Table A4.1 are used.

Table A4.1. Conduction parameters [2], [3]

	k [W/m-K]	δ [cm]
Gallium	41	1
BN liner	36	0.32
Cell wall	17	0.54

Note that substituting (A4.3) in (A4.1) determines the surface temperature  $T_s$  only implicitly. In any case, the effective cell surface area A is determined by fitting (A4.1) to cooling data obtained in Tests 1-3. Actual heat loss rates from the cell are estimated using cell temperature vs. time data for times t > t' during which there is no electrode, plasma or EMP power generation. Using energy conservation and ignoring differences in temperature between cell parts during this cooldown phase yields

$$\dot{Q}_{\text{Loss, C+R}} = -\left(\sum_{\text{Cell}} m_j C_{pj}\right) \frac{dT_{\text{Cell}}}{dt}$$

where it has been assumed that the electrical cables have been disconnected. Using this approach the data tabulated in Table A4.2 were obtained. Using these data the cell surface area

 $A = 0.227 \text{ m}^2 = 2270 \text{ cm}^2$  resulted in a good fit to (A4.1). The resulting plot of (A4.1) and the fit to the data in Table A4.2 are shown in Fig. 3.

	$T_{Cell}$ [°C]	$\Sigma m_j C_{pj} [kJ/K]$	$dT_{Cell}/dt$ [°C/s]	$\dot{Q}_{Loss, C+R}$ [kW]
Test 1	290	3.749	-0.380	1.425
Test 2	450	3.749	-1.060	3.972
Test 3	415	3.749	0.670	2.511

Table A4.2. Measured cell heat loss rates

Having resolved each parameter in (A4.1) yields the rate of cell heat loss as a function of cell surface temperature:  $\dot{Q}_{Loss, C+R}(T_s)$ . However, to determine the net loss of energy from the cell by convection and radiation in a test,

$$Q_{\text{Loss, C+R}} = \int_{t_0}^{t_1} \dot{Q}_{\text{Loss, C+R}}(T_{\text{Cell}}) dt$$

it is useful to have the loss rate in terms of the cell temperature because it is this temperature that is measured in the test. This was done by re-plotting (A4.1) in terms of  $T_{Cell}$  (knowing the relation between  $T_s$  and  $T_{Cell}$ ), and then finding an empirical fit to this curve, as shown in Fig. A4.1.

![](_page_29_Figure_6.jpeg)

Figure A4.1. Curve fit for  $\dot{Q}_{Loss, C+R}(T_{Cell})$ 

# Appendix 5. Energy balance data tables

Test 1: Stat	ion 6A (0311	120)												
Times			Cell temp	eratures			Bath wate	r temperat	ures		Temperat	ure-time g	radients	
t <sub>o</sub> [s]	313		T <sub>cello</sub> [°C]		39.67		T <sub>w1(1)</sub> [°C]		37.010		(dT <sub>w</sub> /dt) <sub>t2</sub>	[°C/s]	8.00E-04	
t' [s]	315.95		T <sub>cell2</sub> [°C]		42.86		T <sub>w1(2)</sub> [°C]		37.009		(dT <sub>cell</sub> /dt)	2 [°C/s]	-0.05	
t <sub>1</sub> [s]	387		(T <sub>Cell2</sub> - T <sub>Cel</sub>	₀) [°C]	3.19		T <sub>w1</sub> [°C]		37.010					
t <sub>2</sub> [s]	610						T <sub>w2(1)</sub> [°C]		37.553		Thermal c	apacities		
(t' - t <sub>o</sub> ) [s]	2.95		Water hea	at capacity	and hvap		T <sub>w2(2)</sub> [°C]		37.545		Cell: Σm <sub>j</sub> C	C <sub>pj</sub> [kJ/K]		3.749
(t <sub>2</sub> - t <sub>1</sub> ) [s]	223		C <sub>pw</sub> [kJ/kg	-K]	4.178		T <sub>w2</sub> [°C]		37.549		Structure:	Σm <sub>k</sub> C <sub>pk</sub> [k.	I/K]	3.297
			h <sub>vap2</sub> [kJ/k	g]	2412.5		(T <sub>w2</sub> - T <sub>w1</sub> )	[°C]	0.539		WJ pump:	m <sub>wJ</sub> C <sub>pWJ</sub> [k	л <b>/</b> к]	1.72
Water mass change					EMP pump power				Gas react	ion enthalp	oy rate			
Scale (initial) [g]		2981			Voltage [	V]	0.3		O <sub>2</sub> [sccm]		200			
Scale (fina	l) [g]		3254			Current [	kA]	0.24		O <sub>2</sub> [mol/s	]	0.000137		
Scale (char	nge) [g]		273	(uncal.)		Power [kW] 0.072			H <sub>2</sub> O [mol/	/s]	0.000273			
Drip loss (o	lry cell) [g]		70	(uncal.)						h <sub>fH2O</sub> [kJ/r	mole]	-241.826		
Evap. rate	[g/min]		0.66	0.66 (uncal.)		Water masses			Σ(mh) <sub>H2,O2,H2O</sub> [kW]		0.066073			
Elapsed tin	ne [min]		65			m <sub>w1</sub> [kg]	126							
Evap. loss	[g]		42.9	(uncal.)		m <sub>w2</sub> [kg]	125.720			Cable los	s rate			
Corrected :	scale change	e [g]	160.1	(uncal.)						Q <sub>Loss,Cables</sub>	[kW]	2		
Calibration	factor, ĸ [1]	]	1.75			Net WJ a	nd bath hea	t loss pow	er					
Net mass c	hange, δm <sub>w</sub>	[g]	-280.175			(P <sub>WJ</sub> - Q <sub>Los</sub>	<sub>ssb</sub> ) [kW]	0.23677						
Net mass c	hange, δm <sub>w</sub>	[kg]	-0.28018											
						- 0								
Enthalpy c	nanges	A field		284 0070		Energy fic	DWS	Tion 1			274.0			
Vacer: m <sub>w</sub>	10 pw (1w2 = 1w	1) [KJ]		675 022		ENAD on or	energy, c <sub>ek</sub>				2/4.3			
	л. оп <sub>w</sub> n <sub>vap2</sub>	1 [6]		11 050		Coll conv	ection and r	adiation k		[ki]	0.212			
Structure:	oj\'cellz <sup>-</sup> 'cell0 ∑m.C. /T	, [Ν] Τ ) [Ι	d1	-6 99294		Coll coble		fkil	JSS, Q <sub>LOSS,C</sub>	R	71.05			
Wi nump:	m C (T	-T )[k	11	0.33234		Cell heat		ables [NJ]			167.55			
ws pump.	WJ CpWJ W2	- 'w1/ [K	·1	0.520		Not W/I p	ump and ba	th loss /E	0	[k]]	52 800			
						Gas react	ion enthalo	v addition	ΣΗ [kJ]	~J	0.195			
Plasma en	ergy, power	and gair	1			Capicall	.e.renanap	, 2001001	20100		0.135			
Plasma en	ergy, E <sub>Plasma</sub> [	[kJ]	805.27											
Plasma pov	wer, P <sub>Plasma</sub> [	kW]	272.97											
Caine /F	+E. \/E	[1]	3 929											

## Energy balance data: Test 1

## Energy balance data: Test 2

Test 2: Stat	tion 6A (031120)												
Times		Cell temp	eratures			Bath wate	r temperat	ures		Temperat	ure-time g	radients	
t <sub>o</sub> [s]	127	T <sub>cello</sub> [°C]		40.05		T <sub>w1(1)</sub> [°C]		34.698		(dTw/dt)t2	[°C/s]	2.10E-04	
ť [s]	140.24	T <sub>cell2</sub> [°C]		40.59		T <sub>w1(2)</sub> [°C]		34.693		(dT <sub>cell</sub> /dt),	2 [°C/s]	-0.0099	
t <sub>1</sub> [s]	188	(T <sub>Cell2</sub> - T <sub>Cel</sub>	<sub>lo</sub> ) [°C]	0.535		T <sub>w1</sub> [°C]		34.696					
t <sub>2</sub> [s]	430					T <sub>w2(1)</sub> [°C]		35.587		Thermal c	apacities		
(t' - t <sub>o</sub> ) [s]	13.24	Water hea	at capacity a	and hvap		T <sub>w2(2)</sub> [°C]		35.588		Cell: Σm <sub>j</sub> C	C <sub>pj</sub> [kJ/K]		3.749
(t <sub>2</sub> - t <sub>1</sub> ) [s]	242	C <sub>pw</sub> [kJ/kg	-K]	4.178		T <sub>w2</sub> [°C]		35.588		Structure:	Σm <sub>k</sub> C <sub>pk</sub> [k	I/K]	3.297
		h <sub>vap2</sub> [kJ/k	g]	2417.2		(T <sub>w2</sub> - T <sub>w1</sub> )	[°C]	0.892		WJ pump:	m <sub>wJ</sub> C <sub>pwJ</sub> [k	л <b>\</b> к]	1.72
Water mas	s change				EMP pump	power			Gas react	ion enthalp	oy rate		
Scale (initial) [g]		2902			Voltage [V	1	0.6		O <sub>2</sub> [sccm]		200		
Scale (final	) [g]	3059			Current [k	A]	0.24		O <sub>2</sub> [mol/s	]	0.000137		
Scale (change) [g]		157	(uncal.)		Power [kW	/]	0.144		H <sub>2</sub> O [mol,	/s]	0.000273		
Drip loss (wet cell) [g] 43		(uncal.)						h <sub>fH2O</sub> [kJ/r	nole]	-241.826			
Evap. rate	vap. rate [g/min] 0.66		(uncal.)		Water masses				$\Sigma(mh)_{H2,O2,H2O}$ [kW]		0.066073		
Elapsed tin	ne [min]	50			m <sub>w1</sub> [kg]	126							
Evap. loss [	[g] 33		(uncal.)		m <sub>w2</sub> [kg]	125.858			Cable loss rate				
Corrected s	scale change [g]	81	(uncal.)						Q <sub>Loss,Cables</sub>	[kW]	2		
Calibration	factor, κ [1]	1.75			Net WJ an	d bath hea	at loss pow	er					
Net mass c	hange, δm <sub>w</sub> [g]	-141.75			(P <sub>WJ</sub> - Q <sub>Loss</sub>	<sub>b</sub> ) [kW]	0.074364						
Net mass c	hange, δm <sub>w</sub> [kg]	-0.14175											
Catholic al					F								
Enthalpy cr	nanges		469 5729		Electrode	ws	[ki]			447.2			
Vaporizatio	$p_{1} \circ p_{W}(1_{W2} - 1_{W1})[K]$		-242 629		EMP opor		lect [NJ]			1 907			
Cell: Sm.C	(T = T =) [k]		2 006		Cell conve	ction and	u radiation lo	oss ()	- [ki]	198.8			
Structure:		) [ki]	-14,7129		Cell cable	loss. O	ester [k]]	, 22), C4LOSS, C4	-R [10]	47.76			
Winump:	mC(T T)	[ki]	1.534		Cell heat l	nss. O	(ki)			246.56			
tto pampi		[10]	1001		Net WI pu	mp and ba	th loss. (E.		[k]]	17,996			
					Gas reactio	on enthalp	y addition,	ΣH [kJ]		0.875			
Plasma ene	ergy, power and g	ain											
Plasma ene	ergy, E <sub>Plasma</sub> [kJ]	579.62											
Plasma pov	wer, P <sub>Plasma</sub> [kW]	43.78											
Gain: (E	+ E)/E [1]	2,296											

## Energy balance data: Test 3

Test 3: Stat	tion 6A (031120)												
Times		Cell temp	eratures			Bath wate	r temperat	ures		Temperat	ure-time g	radients	
t <sub>o</sub> [s]	543	T <sub>cello</sub> [°C]		37.49		T <sub>w1(1)</sub> [°C]		34.334		(dT <sub>w</sub> /dt) <sub>t2</sub>	[°C/s]	4.60E-04	
t' [s]	546.44	T <sub>cell2</sub> [°C]		39.67		T <sub>w1(2)</sub> [°C]		34.340		(dT <sub>cell</sub> /dt),	2 [°C/s]	0.025	
t <sub>1</sub> [s]	612	(T <sub>cell2</sub> - T <sub>cel</sub>	<sub>o</sub> ) [°C]	2.18		T <sub>w1</sub> [°C]		34.337					
t <sub>2</sub> [s]	840					T <sub>w2(1)</sub> [°C]		35.252		Thermal c	apacities		
(t' - t <sub>o</sub> ) [s]	3.44	Water hea	at capacity	and hvap	T <sub>w2(2)</sub> [°C]			35.253	Cell: Σm <sub>j</sub> C <sub>pj</sub> [kJ/K]		<sub>pi</sub> [kJ/K]		3.74
(t <sub>2</sub> - t <sub>1</sub> ) [s]	228	C <sub>pw</sub> [kJ/kg-K]		4.178		T <sub>w2</sub> [°C]		35.253		Structure: $\Sigma m_k C_{pk}$ [kJ,		I/K]	3.29
		h <sub>vap2</sub> [kJ/k	g] 2418.0	)	(T <sub>w2</sub> - T <sub>w1</sub> )	[°C]	0.915		WJ pump: m <sub>wJ</sub> C <sub>pwJ</sub> [		kJ/K]	1.72	
Water mass change					EMP pump power				Gas reaction enthalpy rate		oy rate		
Scale (initial) [g]		2880			Voltage [V	1	0.59		O <sub>2</sub> [sccm]		200		
Scale (final) [g]		3035			Current [kA]		0.252		O <sub>2</sub> [mol/s]		0.000137		
Scale (char	Scale (change) [g]		(uncal.)		Power [kW	/]	0.14868		H <sub>2</sub> O [mol/s]		0.000273		
Drip loss (wet cell) [g]		43	(uncal.)						h <sub>fH20</sub> [kJ/mole]		-241.826		
Evap. rate [g/min]		0.66	(uncal.)		Water masses				Σ(mh) <sub>H2,O2,H2O</sub> [kW] 0.		0.066073		
Elapsed time [min]		50			m <sub>w1</sub> [kg]	126							
Evap. loss [g]		33	(uncal.)		m <sub>w2</sub> [kg] 125.862				Cable loss rate				
Corrected scale change [g]		79	(uncal.)						Q <sub>Loss,Cables</sub>	[kW]	2		
Calibration	n factor, κ [1]	1.75			Net WJ an	d bath hea	t loss pow	er					
Net mass change, δm <sub>w</sub> [g] -:		-138.25			(P <sub>WJ</sub> - Q <sub>Loss</sub>	<sub>b</sub> ) [kW]	0.337924						
Net mass c	hange, δm <sub>w</sub> [kg]	-0.13825											
Cath allowed					F								
Enthalpy changes		401 0440		Electrodo	ws	[ki]			451.0				
Vanorization: ôm h _ [k]			-33/ 200		EMP energ		ect L <sup>NU</sup> J			0.511			
Cell: $\Sigma m.C.(T_{a,m}, T_{a,m})$ [k]			8,173		Cell convection and radiation loss			55. O	- [ki]	198.9			
Structure: $\Sigma m_{i}C_{i}(T_{i}, z - T_{collo}) [k]$			-7.37704		Cell cable loss, Que estin [k]				FR 1103	65.56			
WJ pump: $m_{WJ}C_{pWJ}(T_{w2} - T_{w1})$ [kJ]			1.575		Cell heat l	DSS. Queres	[k]]			264.46			
			2.070		Net WI nu	mp and ha	th loss. (E.	loss. (Fuu - Quus) [k]]		77.047			
					Gas reactio	reaction enthalpy addition.			ΣH [kJ]				
Plasma en	ergy, power and g	ain											
Plasma energy, E <sub>Plasma</sub> [kJ] 553.38													
Plasma power, P <sub>Plasma</sub> [kW] 160.87													
Gain: (E.	+ E [1]	2,225											