INTRODUCTORY CHEMICAL DYNAMICS—USING THE CHEMICAL POTENTIAL FROM THE START

An Informal Introduction to Chemical Processes

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Universidad de La Habana, January 26–30, 2009
THE GOAL OF THIS TALK...

Traditionally, it is assumed that the chemical potential can only be introduced—and understood—as a derived quantity.

In this talk, I would like to motivate the view that the chemical potential is one of the quantities we should take as primitive, meaning, as fundamental, basic, not derivable and not derived from other (seemingly) more fundamental concepts.

Any discussion of such a point—why should we introduce a particular quantity as primitive, and how can we do this?—has emotional quality. Therefore, I will use a good part of my presentation to motivate the concept of chemical potential by discussing basic human conceptualizations of nature. These conceptualizations have been identified in recent research in cognitive science in general, and cognitive linguistics in general. They will then be applied to chemical processes leading to the identification of the chemical potential as a measure of the intensity of chemical processes.
LITERATURE


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Part 1

**INTRODUCTION: CHEMICAL PROCESSES**

Chemical processes are those that deal with the **quantity** of substances, their strength or **intensity** relative to each other, and their **power** to cause other phenomena...
# Word Models of Chemical Phenomena

<table>
<thead>
<tr>
<th>Example</th>
<th>A Word Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmosis in potatos</td>
<td>Should you cook potatoes in <em>lightly</em> salted water or in <em>strongly</em> salted water? It turns out that in fresh water, potatoes swell, in strongly salted water they shrink. Water <em>flows</em> into or out of the potatoes: it <em>forced</em> from places where it is purer to be where there is more stuff dissolved in it. So what is the best way to cook potatoes? Shouldn’t we try to avoid a major exchange of water by using just the <em>right amount</em> of salt? If we want to leave the roots in their original state, we should try to go for a sort of <em>balance</em> between the inside of the potatoes and their environment.</td>
</tr>
<tr>
<td>Melting of ice</td>
<td>The substance H2O <em>transforms</em> from liquid to solid if the temperature of the environment is below 0°C, and it has a <em>tendency</em> to go from solid to liquid if it is warm. It seems, H2O “<em>likes</em>” to be in the liquid state when it is warm, and it “prefers” to be in the solid state when it is cold. There is a point of <em>balance</em> between liquid and solid at 0°C.</td>
</tr>
</tbody>
</table>
### Example

| Detergents and washing clothes | Want to clean dirty clothes? Depending on the type of stains, you might need some **aggressive** soap, in other cases, a **mild** detergent should be enough. Some soaps are more **powerful** than others. Clearly, if you have more clothes to wash, you need **more** detergent. |
| Batteries | In batteries, chemicals are brought in contact in such a way that electricity flows when they react. The **intensity** of the reaction—which depends upon the particular chemicals—determines the electric potential difference, i.e., the electric “**tension**.” **More** of the same chemicals allow the battery to live longer, i.e., to pump more charge. The **kind** and the **quantity** of chemicals determine the **power** of a battery. |
| Burning fuels | Fuels produce heat when burned. If we want more heat, we need **more** fuel, or a better (“**stronger**”) fuel. The **power** of heating depends upon the type of fuel and how fast the fuel is burned. |
Part 2

CONCEPTUALIZATION OF PROCESSES—FORCE DYNAMIC GESTALTS

Human perception leads to the abstraction of a structured gestalt of experiences as diverse as love, pain, heat, or motion. The aspects of the gestalt are quantity, intensity, and power/force. I call them *Force Dynamic Gestalts*.

Quantity, intensity, and power (and associated schemas such as driving force, flow, container, resistance, balance…) are the basic concepts of a continuum physics approach to natural phenomena.
THE FORCE DYNAMIC GESTALT OF ABSTRACT CONCEPTS

Concepts such as evil or love or thought are abstracted from experience in the form of a preconceptual structured Force Dynamic Gestalt having the aspects of

Substance (quantity) / Intensity (quality) / Force or Power

Linguistic expressions for evil:

• She had no idea how strong evil could be.
• Evil burned intensely.
• Evil grew amongst us.
• Evil gained control of this group of people.
• Slowly, evil left his soul.
• Evil made him do things he would not have done otherwise.

Entailments of the conceptualization

Two bad people means double the evil. More evil means higher intensity. More evil means it is more powerful. Higher intensity of evil increases its power.
THE METAPHORIC CONCEPTUALIZATION OF MUSIC


- The moving music metaphor (“Here comes the recapitulation.”). **Object**
- The musical landscape metaphor (“The melody rises up ahead.”). **intensity**
- Music as moving force metaphor (“This piece moved me to tears”). **Force or power**

Slowly with expression

Some-where o-ver the rain-bow way up high,

there’s a land that I heard of once in a lull-a-by.
EVIDENCE FOR THE GESTALT OF PHYSICAL PROCESSES 1

Persons are asked if they agree or disagree with certain expressions

- The temperature is high
- Today, the heat is high
- There is lots of heat in this room
- There is lots of temperature in this room
- Heat drives the engine
- Temperature drives the engine

Agreement with classes of expressions\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>as substance</th>
<th>as level</th>
<th>as cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat</td>
<td>0.67 (1)</td>
<td>0.14 (0)</td>
<td>0.77 (1)</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.09 (0)</td>
<td>0.83 (1)</td>
<td>0.09 (0)</td>
</tr>
</tbody>
</table>

\(^a\) Agreement (1) or disagreement (0) with expressions using heat and temperature. Expected results in parentheses. Results of a questionnaire given to journalism students in Summer of 2004.
The concept of heat of the members of the Accademia del Cimento: Saggi di naturali esperienze... (1667)

M. Wiser and S. Carey (1983): When Heat and Temperature were one.

“The Experimenters’ concept of heat had three aspects: substance (particles), quality (hotness), and force.”

A weakly differentiated gestalt

It seems that the Experimenters did not really distinguish between these aspects of the gestalt of heat.
Sadi Carnot (1796-1832)
Réflexions sur la puissance motrice du feu

D'après les notions établies jusqu'à présent, on peut comparer avec assez de justesse la puissance motrice de la chaleur à celle d'une chute d'eau [...]. La puissance motrice d'une chute d'eau dépend de sa hauteur et de la quantité du liquide; la puissance motrice de la chaleur dépend aussi de la quantité de calorique employé, et de ce qu'on pourrait nommer, de ce que nous appellerons en effet la hauteur de sa chute, c'est-à-dire de la différence de température des corps entre lesquels se fait l'échange du calorique.
The Force Dynamic Gestalt of Physical Processes

Human perception of phenomena such as fluids, electricity, heat, motion

The concept of “heat,” for example, is abstracted by perception from the sum total of thermal experiences in the form of a gestalt: An entity that is simpler than the sum of its parts. While we do not differentiate a gestalt of a collective of phenomena (such as electricity or heat) consciously, we do notice aspects. The most fundamental aspects humans use to talk about such a gestalt are

Table 1: The Force Dynamic Gestalt of collectives of physical phenomena

<table>
<thead>
<tr>
<th>Aspect of Gestalt</th>
<th>Metaphoric Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity (quality)</td>
<td>Polarity such as light-dark, warm-cold, high-low, fast-slow, strong-weak. The concepts are structured metaphorically by the image schema of verticality (intensity as a level).</td>
</tr>
<tr>
<td>Quantity (substance)</td>
<td>Substance-like (or fluid-like) concepts are metaphorically structured in terms of the image schema of fluid substances.</td>
</tr>
<tr>
<td>Force or power</td>
<td>Prototypical causation as the gestalt of direct manipulation.</td>
</tr>
</tbody>
</table>
Metaphors and analogical reasoning

*Origin and meaning of analogies*

When different domains of experience are structured metaphorically by the same source domains (such as by the same image schemas), these domains become comparable (they are looking similar).

This comparison can be applied in the construction of analogies. An analogy is a double-sided mapping (more or less symmetrical).
ENTAILMENTS OF THE FORCE DYNAMIC GESTALT OF PHYSICAL CONCEPTS

An example of entailments that can be brought into quantitative form

Power =

Level difference \times \text{Current of substance}

\[ Power = \frac{1}{2} \mu m g h \]

Energy is released

\[ I_m \]

\[ \varphi_1 \]

\[ \varphi_2 \]
THE WATERFALL IMAGE IN PROCESS DIAGRAMS

- Ideal coupling

- Real coupling
ENERGY FLOW AND STORAGE IN PROCESS DIAGRAMS

• Transport of energy

• Energy storage
**Energy in Thermal Processes**

**Thermal power** = Temperature difference · Entropy current

**Energy current in heating and cooling** = Temperature · Entropy current

**Dissipation rate** = Temperature · Entropy production rate
Part 3

CONCEPTUALIZING CHEMICAL PROCESSES

Chemical processes are those that deal with the quantity of substances, their strength or intensity relative to each other, and their power to cause other phenomena…

It appears quite reasonable to assume that chemical processes are conceptualized with the help of the same Force Dynamic Gestalt that proved its utility in other processes…
## Motivating the Concept of Chemical Potential and Chemical Driving Force

<table>
<thead>
<tr>
<th></th>
<th>Observation and explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air and Water</strong></td>
<td>When dry air flows over warm water, the air picks up water (vapor). There is a <strong>driving force</strong> for the transfer of water into the (dry) air.</td>
</tr>
<tr>
<td><strong>Water and Ice</strong></td>
<td>At a temperature of 25°C, water does not turn to ice, ice turns to water: H2O “likes better” to be in the liquid state. At a temperature of 0°C, there is neither a tendency for water to turn into ice nor a tendency for ice to turn into water: we have a state of <strong>equilibrium</strong>.</td>
</tr>
<tr>
<td><strong>Producing Metal Sulfides</strong></td>
<td>When Mg (magnesium), Zn (zinc), iron (Fe), and copper (Cu) are made to react with sulfur (S), metal sulfides are produced. The intensity of the reactions is very different, with Mg the most violent, and Cu the least active. Clearly, we need a measure of <strong>intensity</strong> (or difference of intensities) to explain this result.</td>
</tr>
<tr>
<td><strong>Burning Fuels</strong></td>
<td>For the same amount of fuel burned, vastly different amounts of heat can be produced: we need a measure of <strong>intensity</strong> of the reaction.</td>
</tr>
<tr>
<td><strong>α-glucose and β-glucose</strong></td>
<td>If there is only α-glucose in an aqueous solution, it turns into β-glucose: there is a <strong>driving force</strong> of the reaction. The <strong>stronger the driving force</strong>, the <strong>faster</strong> the reaction. If the anomers are in a particular proportion (roughly 40:60), there is no conversion: we have <strong>equilibrium</strong>.</td>
</tr>
</tbody>
</table>
MOTIVATING THE CONCEPT OF CHEMICAL POTENTIAL AND CHEMICAL DRIVING FORCE

Mutarotation of glucose

Toluene in water and air

Volume of red blood cells in an aqueous solution
## Analogies: Substance-like Quantities, Potentials, and Power

<table>
<thead>
<tr>
<th>Subsystem</th>
<th>Substance-like quantity</th>
<th>Current of quantity</th>
<th>Production rate</th>
<th>Associated power</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydraulics</strong></td>
<td>Volume of liquid</td>
<td>Volume current</td>
<td></td>
<td>$P = \Delta p I_V$</td>
</tr>
<tr>
<td><strong>Electricity</strong></td>
<td>Electric charge</td>
<td>Current of charge</td>
<td></td>
<td>$P = \Delta \varphi_{el} I_Q$</td>
</tr>
<tr>
<td><strong>Thermodynamics</strong></td>
<td>Entropy</td>
<td>Entropy current</td>
<td>Entropy production rate</td>
<td>$P = \Delta T I_S$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\mathcal{P}_{diss} = T I_S$</td>
</tr>
<tr>
<td><strong>Rotation</strong></td>
<td>Angular momentum</td>
<td>Angular momentum current</td>
<td></td>
<td>$P = \Delta \omega I_V$</td>
</tr>
<tr>
<td><strong>Translation</strong></td>
<td>Momentum</td>
<td>Momentum current</td>
<td></td>
<td>$P = \Delta v I_V$</td>
</tr>
<tr>
<td><strong>Gravitation</strong></td>
<td>(gravitational) mass</td>
<td>Current of mass</td>
<td></td>
<td>$P = \Delta \varphi_g I_m$</td>
</tr>
<tr>
<td><strong>Chemistry</strong></td>
<td>Amount of substance</td>
<td>Current of amount of substance</td>
<td>Production rate of $n$</td>
<td>$P = \Delta \mu I_n$ $P = \Delta \mu \Pi_n$</td>
</tr>
</tbody>
</table>
Process diagram of a battery, including production of entropy.

There is no energy transfer relative to the system with chemical substances.

Energy released in the reactions comes from energy storage.

The power of the chemical process is split between the electrical and thermal processes.

\[ P_{\text{chem}} = \left[ \Delta \mu \right]_R \Pi_n \]
THE CHEMICAL DRIVING FORCE

REACTION:

\[ \nu_1 A_1 + \nu_2 A_2 + \ldots \leftrightarrow \zeta_1 B_1 + \zeta_2 B_2 + \ldots \]

DRIVING FORCE:

\[ [\Delta \mu]_R = \zeta_1 \mu_{B_1} + \zeta_2 \mu_{B_2} + \ldots - (\nu_1 \mu_{A_1} + \nu_2 \mu_{A_2} + \ldots) \]

Voluntary process \[ [\Delta \mu]_R < 0 \]

Involuntary process \[ [\Delta \mu]_R > 0 \]

Chemical equilibrium \[ [\Delta \mu]_R = 0 \]
System dynamics model diagram of chemical processes involving a species whose amount of substance \( n \) is tracked as a function of time.

There are two processes: Inflow/outflow of the species (with respect to a control volume), and reaction of the species with another one (2) in the control volume.

Both processes are controlled by appropriate chemical potential differences.

\[
\Pi_n = \frac{1}{R_n} \left[ \Delta \mu \right]_R
\]

\[
I_n = G_n \left[ \Delta \mu \right]_R
\]
Part 4

SOME PAPER-AND-PENCIL EXAMPLES

If we have tables of chemical potentials at our disposal, we can easily treat many interesting and real-life applications on the back of an envelope...
# Values of Chemical Potentials and Temperature and Pressure Coefficients

<table>
<thead>
<tr>
<th>Formula</th>
<th>Substance</th>
<th>Chemical potential/ kG\textsuperscript{a}</th>
<th>Temp.coeff. $\alpha_m$ / G/K</th>
<th>Pressure coeff. $\beta_m$ / $\mu$G/Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (s)\textsuperscript{b}</td>
<td>Carbon</td>
<td>0</td>
<td>– 5.69</td>
<td>5.4</td>
</tr>
<tr>
<td>C2H2 (g)</td>
<td>Ethyne</td>
<td>209.20</td>
<td>– 200.83</td>
<td></td>
</tr>
<tr>
<td>CH4 (g)</td>
<td>Methane</td>
<td>– 50.89</td>
<td>– 186.10</td>
<td>24465</td>
</tr>
<tr>
<td>CH4O (l)</td>
<td>Methanol</td>
<td>– 166.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C7H8 (g)</td>
<td>Toluene</td>
<td>122.39</td>
<td>– 319.70</td>
<td></td>
</tr>
<tr>
<td>C7H8 (l)</td>
<td></td>
<td>110.61</td>
<td>– 219.00</td>
<td></td>
</tr>
<tr>
<td>CaCO3 (s)</td>
<td>Calcium carbonate</td>
<td>– 1128.76</td>
<td>– 92.88</td>
<td>36.92</td>
</tr>
<tr>
<td>Cl\textsuperscript{–} (aq)</td>
<td>Chlorine ion</td>
<td>– 131.26</td>
<td>– 56.48</td>
<td>18.0</td>
</tr>
<tr>
<td>CO2 (g)</td>
<td>Carbon dioxide</td>
<td>– 394.40</td>
<td>– 213.68</td>
<td>24465</td>
</tr>
<tr>
<td>CO2 (aq)</td>
<td></td>
<td>– 385.99</td>
<td>– 113.00</td>
<td></td>
</tr>
<tr>
<td>Fe (s)</td>
<td>Iron</td>
<td>0</td>
<td>– 27.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Fe2O3 (s)</td>
<td>Iron oxide</td>
<td>– 743.58</td>
<td>– 87.4</td>
<td>30.4</td>
</tr>
<tr>
<td>FeS (s)</td>
<td>Iron sulfide</td>
<td>– 100.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2 (g)</td>
<td>Hydrogen</td>
<td>0</td>
<td>–131</td>
<td>24465</td>
</tr>
<tr>
<td>Formula</td>
<td>Substance</td>
<td>Chemical potential/ kGa</td>
<td>Temp.coeff. αm / G/K</td>
<td>Pressure coeff. βm / μG/Pa</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------------------</td>
<td>-------------------------</td>
<td>----------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>H2O (g)</td>
<td>Water</td>
<td>– 228.60</td>
<td>– 188.72</td>
<td>24465</td>
</tr>
<tr>
<td>H2O (l)</td>
<td></td>
<td>– 237.18</td>
<td>– 69.91</td>
<td>18.07</td>
</tr>
<tr>
<td>H2O (s)</td>
<td></td>
<td>– 236.59</td>
<td>– 44.77</td>
<td>19.73</td>
</tr>
<tr>
<td>MgS (s)</td>
<td>Magnesium sulfide</td>
<td>– 341.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH3 (g)</td>
<td>Ammonia</td>
<td>–16.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na+ (aq)</td>
<td>Sodium ion</td>
<td>– 261.89</td>
<td>– 58.99</td>
<td>– 1.6</td>
</tr>
<tr>
<td>NaCl (s)</td>
<td>Table salt</td>
<td>– 384.03</td>
<td>– 72.13</td>
<td>27.02</td>
</tr>
<tr>
<td>O2 (g)</td>
<td>Oxygen</td>
<td>0</td>
<td>– 205.02</td>
<td>24465</td>
</tr>
<tr>
<td>O2 (aq)</td>
<td></td>
<td>16.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbSO4 (s)</td>
<td>Lead sulfate</td>
<td>– 813.20</td>
<td>– 148.57</td>
<td>48.2</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
<td>0</td>
<td>–18.82</td>
<td></td>
</tr>
<tr>
<td>SiO2 (s)</td>
<td>Silicon dioxide (α-quartz)</td>
<td>–856.7</td>
<td>– 41.84</td>
<td>22.6</td>
</tr>
<tr>
<td>ZnS (s)</td>
<td>Zinc sulfide</td>
<td>– 201.29</td>
<td>– 57.74</td>
<td>23.89</td>
</tr>
</tbody>
</table>

a. At standard conditions: 298.15 K, 101,325 Pa, pure or 1 mole/l.
b. (s) solid, (l) liquid, (g) gaseous, (aq) aqueous
## SOME EXAMPLES

<table>
<thead>
<tr>
<th>Observation and explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Can hydrogen gas and oxygen gas react spontaneously?</strong></td>
</tr>
<tr>
<td><strong>Why does magnesium react more violently with sulfur than does iron?</strong></td>
</tr>
</tbody>
</table>
At what temperature should water and ice be in equilibrium?

At 25°C, the chemical potential of ice (–236.59 kG) is higher than that of water (–237.18 kG): ice turns to water.

The chemical potentials change with temperature, they increase when the temperature decreases. The temperature coefficient for water (–69.91 G/K) has a greater magnitude than that of ice (–44.77 G/K).

If we apply linear changes, the chemical potentials become equal at 1.5°C:

$$\mu_{\text{Water}} \left(p_0, T_0\right) + \alpha_{\text{Water}} \left(T - T_0\right) = \mu_{\text{Ice}} \left(p_0, T_0\right) + \alpha_{\text{Ice}} \left(T - T_0\right)$$

How much entropy is produced when hydrogen and oxygen react by burning?

The chemical driving force of the reaction

H2 + 0.5 O2 —> H2O

is –237 kG. The energy released in the burning of 1 mole of H2 is therefore equal to $W_{\text{chem}} = 237 \text{ kJ}$. If the reaction were to take place at 25°C (or if we let the reactants cool to this temperature after the reaction), we get an amount of entropy produced equal to

$$S_{\text{prod}} = \frac{W_{\text{chem}}}{T} = 795 \text{ J/K}.$$
| How much CO₂ can be dissolved in bottled water at a pressure of 2 bar? | In equilibrium, the chemical potentials of CO₂ dissolved in bottled water and of pure CO₂ gas in the top part of the bottle. The chemical potential of the gas depends upon its pressure:

\[ \mu(p, T) = \mu(p_0, T) + RT \ln\left(\frac{p}{p_0}\right) \]

The chemical potential of dissolved CO₂ depends upon its concentration:

\[ \mu(c, T) = \mu(c_0, T) + RT \ln\left(\frac{c}{c_0}\right) \]

Setting the first equal to the second at stated conditions, we obtain 0.10 mole/L for the concentration of dissolved CO₂. |
| --- | --- |
| How can the voltage of an electrochemical cell converting hydrogen and oxygen to water (1.23 V) be used to determine the chemical potential of water? | Consider the balance of energy released in the reaction and the energy used in transferring charge through an electric potential difference:

\[
\begin{align*}
U_{\text{Cell}}I_Q &= [\Delta \mu]_R \Pi_n \\
\left[\Delta \mu\right]_R &= \frac{U_{\text{Cell}}I_Q}{\Pi_n} = \frac{U_{\text{Cell}}2eN_0\Pi_n}{\Pi_n} \\
&= 1.23 \times 10^{-19} \times 6.02 \times 10^{23} \text{ J/mole} = 237 \text{ kJ/mole}
\end{align*}
\]
Part 5

Examples of Dynamical Models

If we conceptualize chemical processes (transports and reactions of substances) as demonstrated before, they can easily be modeled as dynamical phenomena...
RED BLOOD CELLS PERMEABILITY

Water

Red blood cell  Impermeable solute  Permeable solute

Vw cell

Mo w

n w inside

kn water

n imp init

c imp inside

c s inside

mu w inside

mu w outside

c imp init

c s 0

In water

In solute

n s inside

kn solute

A

Cell volume / m^3

Time / s

7.8E-17

8.0E-17

8.2E-17

8.4E-17

8.6E-17

8.8E-17

7.8E-17

1 2 3 4 5

8.0E-17

8.2E-17

8.4E-17

8.6E-17

8.8E-17

7.8E-17

1 2 3 4 5

8.0E-17

8.2E-17

8.4E-17

8.6E-17

8.8E-17

7.8E-17

1 2 3 4 5
MUTAROTATION OF GLUCOSE

Diagram of system dynamics model of mutarotation

Experimental data and simulation of model

<table>
<thead>
<tr>
<th>V</th>
<th>mu alpha</th>
<th>delta chem pot</th>
<th>mu beta</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance</td>
<td>Pi n alpha</td>
<td>Pi n beta</td>
<td>Reaction rate</td>
<td>V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amount of substance / mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
</tr>
<tr>
<td>0.008</td>
</tr>
<tr>
<td>0.006</td>
</tr>
<tr>
<td>0.004</td>
</tr>
<tr>
<td>0.002</td>
</tr>
<tr>
<td>0.000</td>
</tr>
</tbody>
</table>

Time / s

0 5000 10000 15000