winmostar tutorial

GAMESS
Redox Potential Calculation

V11.6.5

16 March 2024 X-Ability Co., Ltd.

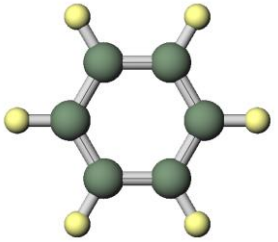
About This Manual

- This manual is a tutorial demonstrating use cases for Winmostar V11.
- For those using Winmostar V11 for the first time, please consult Beginner's Guide.
- For those who wish to explore the details of each feature, please refer to Winmostar User Manual.
- Those who wish to practice the contents of this manual are encouraged to attend a training session.
  - Winmostar Introductory Training Session:This guide only introduces the operation methods of the Basic Tutorial.
  - Winmostar Basic Training Session:We will cover the theoretical background, explanations on interpreting results, operational methods of the Basic Tutorial, and procedures for some tutorials beyond the basic level.
  - Individual Training Session:You can freely customize the training content according to your preferences.
- If you are unable to proceed with the operations as outlined in this manual, please first consult Frequently asked questions.
- If your issue is not resolved through the Frequently Asked Questions, for the purpose of information accumulation and management, please contact us using Contact page. Attach files generated at the time of the issue and provide steps to reproduce the problem.
-

Overview

Using GAMESS with the SMD method to include solvent effects, this tutorial calculates the redox potential of C_6H_6 (benzene)/$C_6H_6^+$ in acetonitrile solution at 25°C, referencing the Ag/AgCl electrode, at the R3LYP/6-311G* level. The SMD method, applied to the optimized structure in vacuum, first involves structure optimization in vacuum, followed by vibrational calculations including solvent effects to compute the free energy. The redox potential is then determined based on Nernst's equation.

$$E_{0/1} = -\left(\frac{G(\text{reduced}) - G(\text{oxidized})}{n_e F}\right) - E_{\text{ABS}}(\text{REF})$$



G(reduced): Gibbs Free Energy of C_6H_6

G(oxidized): Gibbs Free Energy of $C_6H_6^+$

E_{ABS}*(REF)*: Reference Electrode Potential (Ag/AgCl) (Using Experimental Values)

n_e: Total Number of Transferred Electrons F: Faraday's Constant

Note:

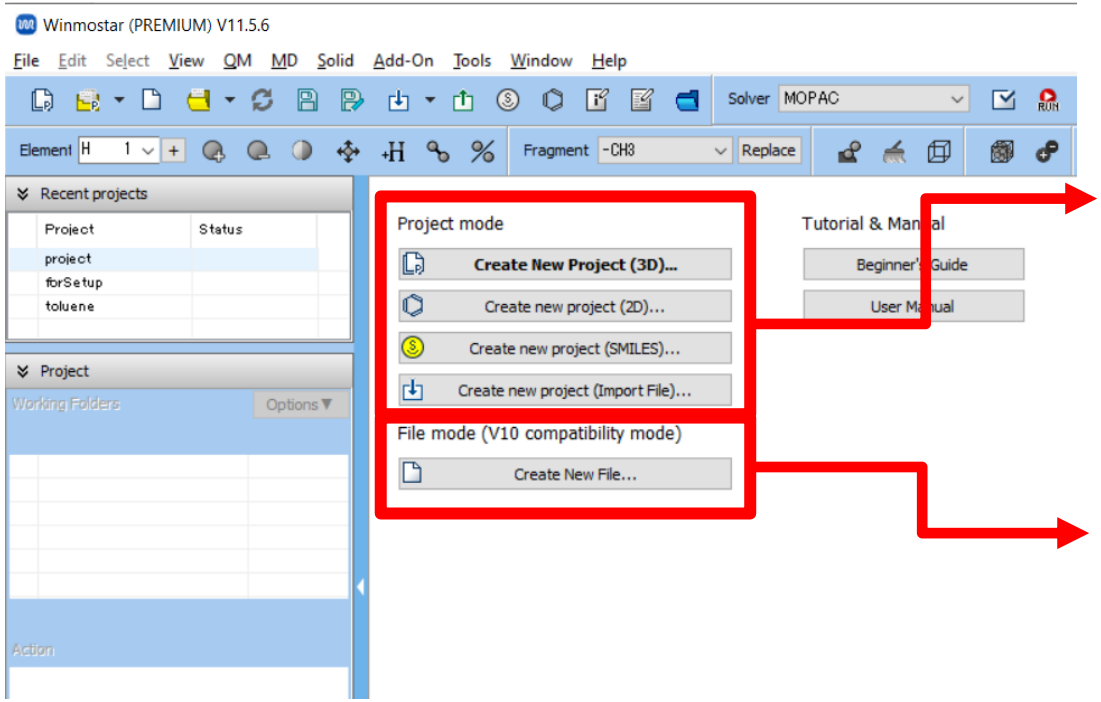
・The calculated redox potential values are influenced by the choice of functional, basis set, and solvent model.

・The calculation formula and the sign of terms may differ according to the literature.

・Attention must be paid to the measurement method and uncertainties of the experimental redox potential values used for comparison.

Operating Modes of Winmostar V11

V11 offers two operating modes: **Project Mode** and **File Mode**.
This manual focuses on operations in Project Mode.
For operations in File Mode, please refer to tutorial for version 10.



Project Mode New Features in V11

Users can manage jobs without having to manage individual files.
We generally recommend using this mode.

File Mode

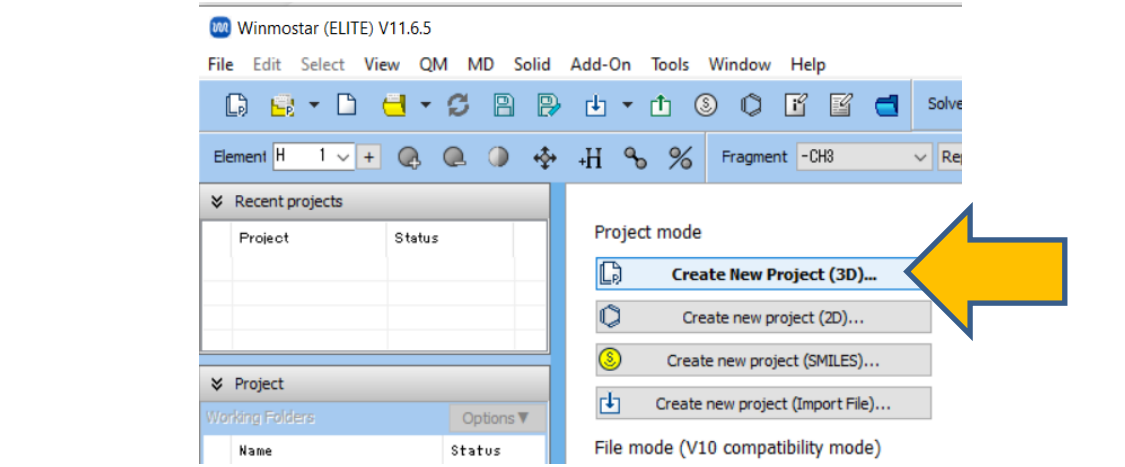
Users explicitly create and manage individual files.
The operational procedure is the same as from V10 and earlier versions.

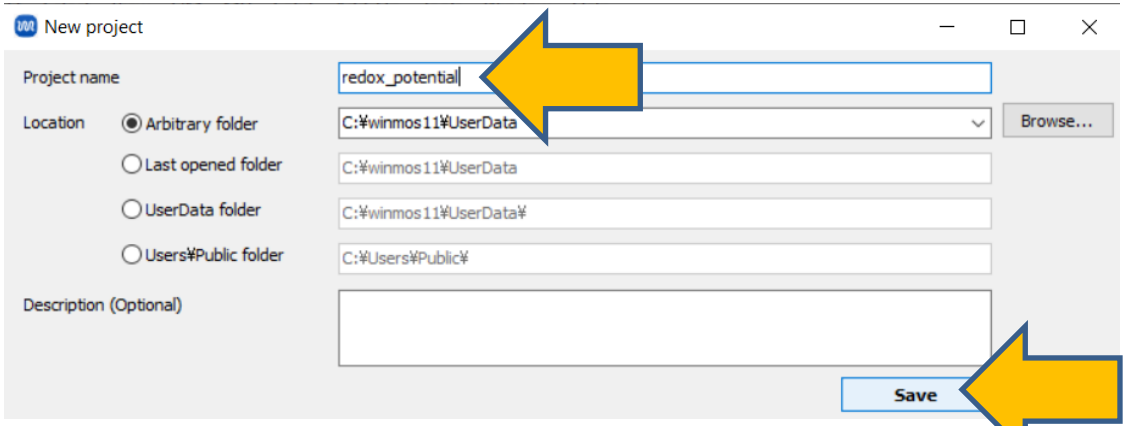
When creating a continuation job, in file mode or versions prior to V10, it is necessary to display the final structure of the original job each time. However, in project mode, the final structure is automatically carried over.

A. Modeling of the System

A. Launch Winmostar and click **Create New Project (3D)**. If Winmostar is already open, click on **File | Close** first.

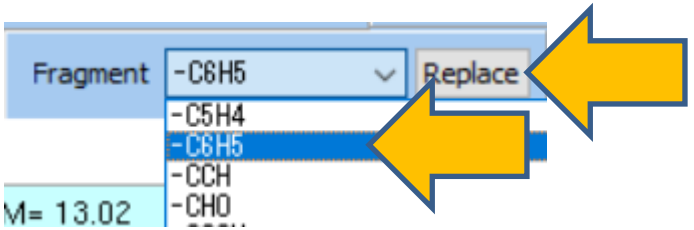
B. Enter '`redox_potential`' as **Project name** and click **Save**.

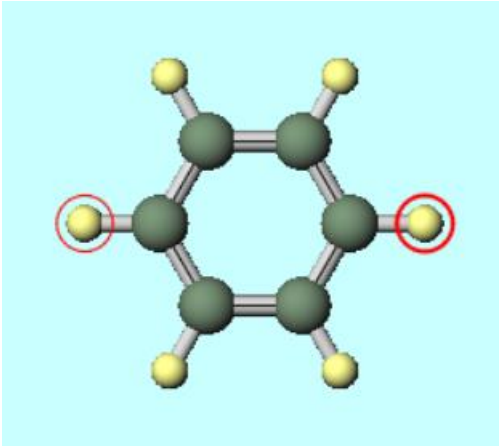




A. Modeling of the System

A. Select **-C6H5** from **Fragment** at the top of Main Window, and click **Replace** once



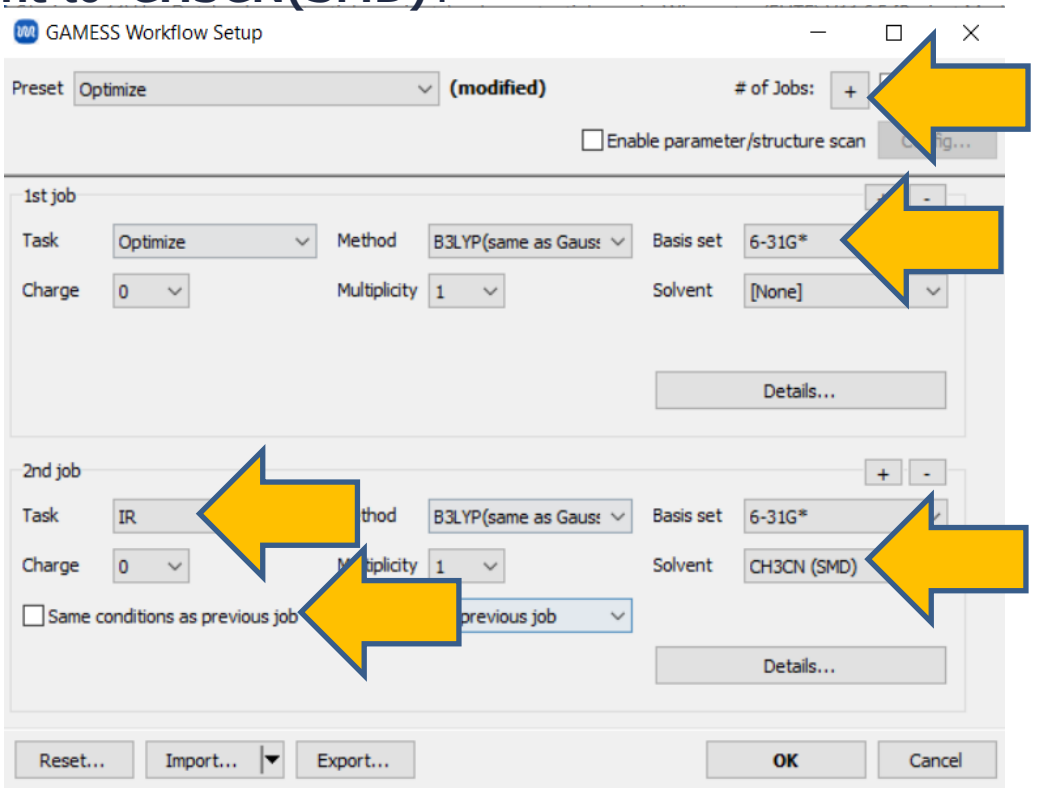


B. Calculation Settings (Structure Optimization + Free Energy Calculation: Zero-valent)

A. Select **GAMESS** from **Solver**, and click **Workflow Setup** button.

B. Change **Basis set** of **1st job** to '**6-311G***', and click **+** button next to **# of jobs** to add **2nd job**.

C. Change **Task** of **2nd job** to '**IR**', uncheck '**Same conditions as previous jobs**', and change **Solvent** to '**CH3CN(SMD)**'.

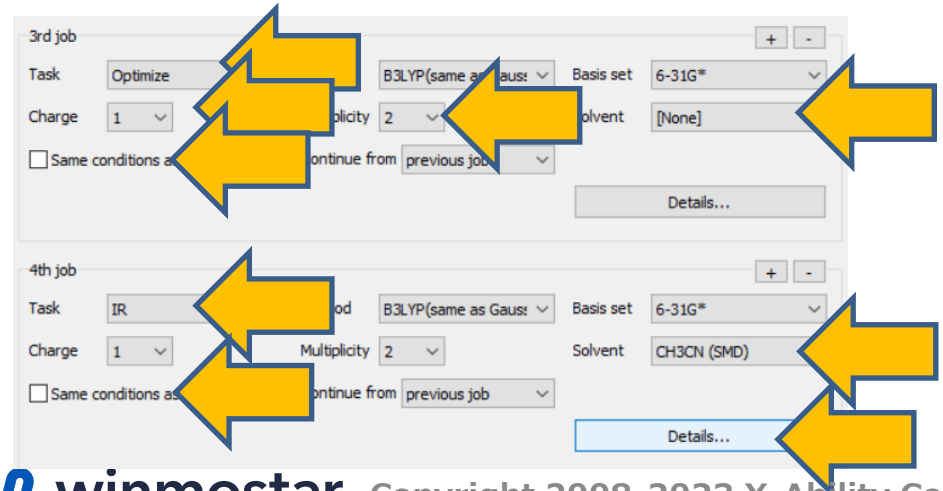


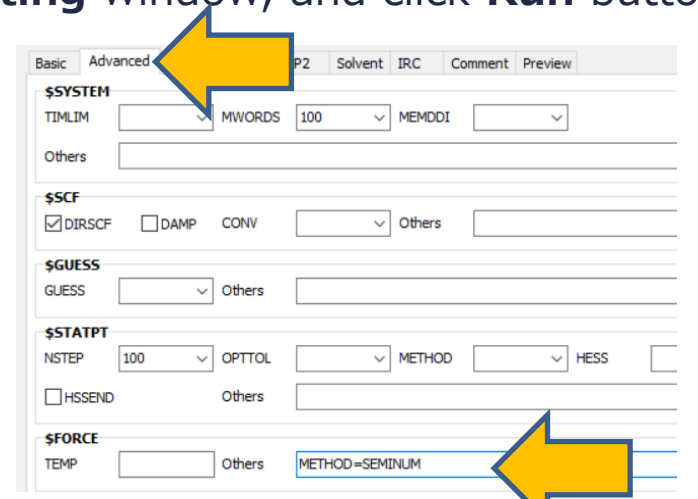
C. Calculation Settings (Structure Optimization + Free Energy Calculation: Monovalent)

A. Click **+** button next to **# of jobs** to add **3rd job**, and change **Task** of **3rd job** to '**Optimize**'. Uncheck '**Same conditions as previous jobs**', change **Charge** to '**1**', **Multiplicity** to '**2**', and **Solvent** to '**[None]**'.

B. Click **+** button next to **# of jobs** to add **4th job**, and change **Task** of **4th job** to '**IR**'. Uncheck '**Same conditions as previous jobs**', and change **Solvent** to '**CH3CN(SMD)**'. Click **Details** button and in **GAMESS Keyword Setup** window's **Advanced tab**, under **$FORCE**, enter '`METHOD=SEMINUM`' in **Others** (since analytic second derivatives are not supported for open-shell systems), and click **OK** button at the bottom right.

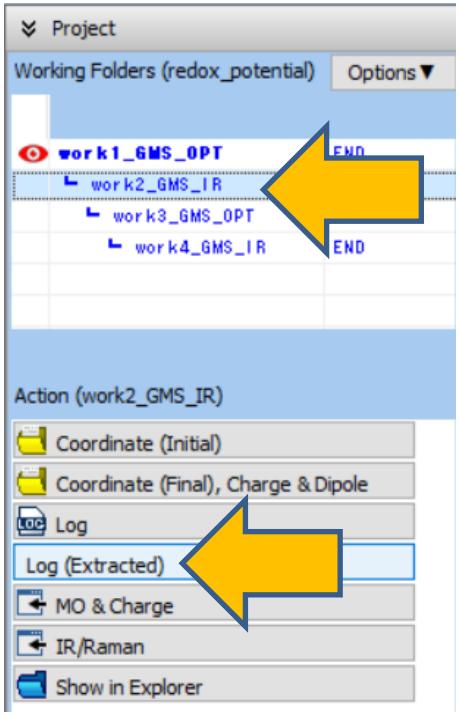
C. Click **OK** button in **GAMESS Workflow Setup** window, set **# of Threads/MPI Proc** according to the computation machine in **Job Setting** window, and click **Run** button.





D. Results Analysis (Calculation of Redox Potential)

A. After the status of work folders **work1 to work4** changes to **END**, click **work2_GMS_IR** in **Working Folders**, and click **Log(Extracted)** in **Action** (click on **Log** for the Professional Economy version). Extract the energy value starting with 'FINAL R-B3LYPV1R ENERGY IS' (the enthalpy at 0K, in Hartree units), and the value under column G for TOTAL (the correction value for Gibbs free energy at 25℃ (=298.15K), in units of kJ/mol).



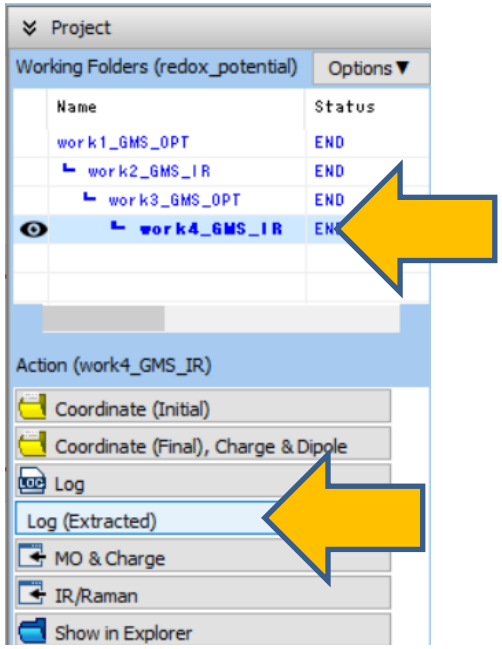
Extracted Log (C:\winmos11\UserData\redox_potential.wmpjdata\work2_GMS_IR\gms.out)

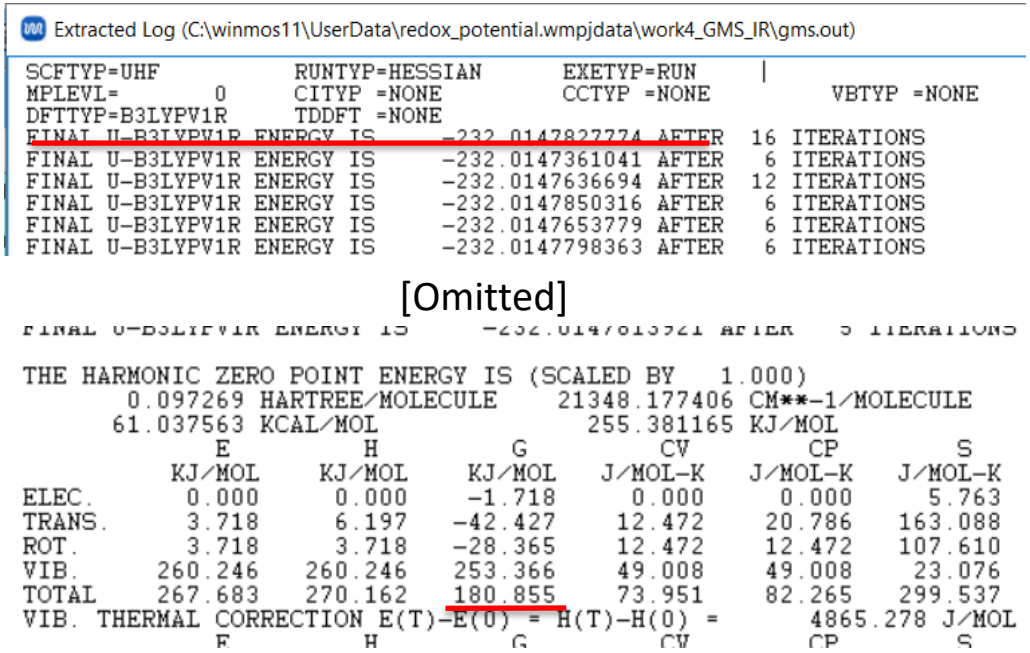
```
         *          GAMESS VERSION = 30 JUN 2023 (R1)          *
EXECUTION OF GAMESS BEGUN 07:36:15 14-MAR-2024
    GBASIS=N31          IGAUSS=       6      POLAR=POPN31
    NDFUNC=       1     NFFUNC=       0     DIFFSP=       F
    NPFUNC=       0      DIFFS=       F     BASNAM=
NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS =  102
NUMBER OF ELECTRONS                          =   42
CHARGE OF MOLECULE                           =    0
SPIN MULTIPLICITY                            =    1
NUMBER OF OCCUPIED ORBITALS (ALPHA)          =   21
NUMBER OF OCCUPIED ORBITALS (BETA )          =   21
TOTAL NUMBER OF ATOMS                        =   12
SCFTYP=RHF          RUNTYP=HESSIAN      EXETYP=RUN
MPLEVL=       0     CITYP =NONE         CCTYP =NONE         VBTYP =NONE
DFTTYP=B3LYPV1R     TDDFT =NONE
FINAL R-B3LYPV1R ENERGY IS     -232.2559342782 AFTER  12 ITERATIONS

THE HARMONIC ZERO POINT ENERGY IS (SCALED BY   1.000)
       0.100738 HARTREE/MOLECULE    22109.359735 CM**-1/MOLECULE
      63.213895 KCAL/MOL             264.486937 KJ/MOL
             E          H          G          CV         CP         S
         KJ/MOL     KJ/MOL     KJ/MOL    J/MOL-K    J/MOL-K    J/MOL-K
ELEC.     0.000      0.000      0.000      0.000      0.000      0.000
TRANS.    3.718      6.197    -42.427     12.472     20.786    163.088
ROT.      3.718      3.718    -28.293     12.472     12.472    107.365
VIB.    268.588    268.588    263.092     46.799     46.799     18.435
TOTAL   276.025    278.504    192.372     71.743     80.057    288.889
VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) =      4101.231 J/MOL
```

D. Results Analysis (Calculation of Redox Potential)

A. Click **work4_GMS_IR** in **Working Folders** and click **Log(Extracted)** in **Action** (click **Log** for the Professional Economy version). Extract the energy value starting with the first 'FINAL U-B3LYPV1R ENERGY IS' (the enthalpy at 0K, in Hartree units) and the value under column G for TOTAL (the correction value for Gibbs free energy at 25℃ (=298.15K), in units of kJ/mol). Since METHOD=SEMINUM is specified in $FORCE, the structure is numerically altered slightly to compute the second derivative numerically. As a result, numerous lines of energy values will be displayed, but the energy of the original structure is the first value.





D. Results Analysis (Calculation of Redox Potential)

- Following the procedure in this book, the redox potential is calculated to be 2.00 V from the formula below. Notably, an experimental value of 2.00 V is reported in reference [1]. **Tools | Unit Converter** was used for unit conversion.

$$E_{0/1} = -\left(\frac{G(\text{reduced}) - G(\text{oxidized})}{n_e F}\right) - E_{\text{ABS}}(\text{REF})$$

	Interpretation	In the Context of This tutorial
G(reduced)	Zero-valent 'Enthalpy at 0K + Gibbs Free Energy Correction at 25°C (298.15K)'	-232.236582 [hartree] = -6.097370623E+005 [kJ/mol] **= -6.097370623E+008 [J/mol]**
G(oxidized)	Monovalent 'Enthalpy at 0K + Gibbs Free Energy Correction at 25°C (298.15K)'	-231.992531 [hartree] = -6.090963065E+005 [kJ/mol] **= -6.090963065E+008 [J/mol]**
n_e	Total number of transferred electrons	**1**
F	Faraday constant	**96485.33289 [C mol^{-1}]**
E_{ABS}(REF)	Ag/AgClReference electrode（+0.199V（vs. SHE,25℃））	**4.639 [V]（25℃）[1]**
$E_{0/1}$	**Redox Potential**	**2.00 [V]**

[1] Handbook of Electrochemistry, 6th Edition

Supplement:
Basis Set Dependency and Reference Electrodes

- In addition to B3LYP/6-311G*, calculations at the B3LYP/6-31G* level yielded potentials as follows, which slightly deviated from the experimental values using the commonly employed 6-31G* basis set.

	Redox Potential [V]
Experimental Value [1]	**2.00**
Calculated Value [B3LYP/6-31G*]	**1.85**
Calculated Value [B3LYP/6-311G*]	**2.00**

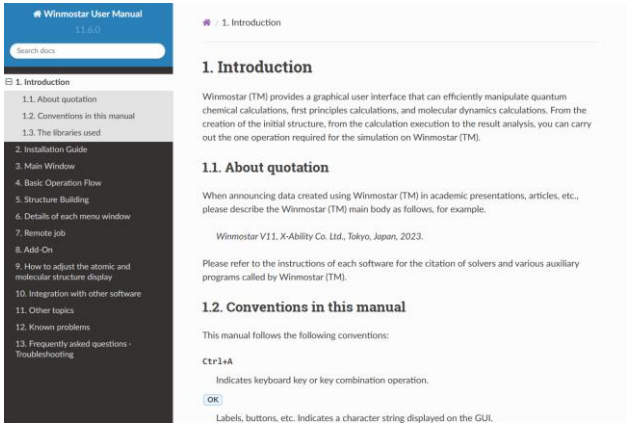
- This tutorial used the Ag/AgCl reference electrode for the experimental values of $C_6H_6/C_6H_6^+$, but if you wish to calculate values for other reference electrodes, use the following values at 25°C from reference [1].

Reference Electrode	Redox Potential [V]
SHE	**4.44**
SCE	**4.6844**
Ag/AgCl	**4.639**

[1] Handbook of Electrochemistry, 6th Edition

Finally

- For detailed information on each feature, please refer to Winmostar User Manual.



Winmostar User Manual

Scenes from Winmostar Training Session

- If you wish to practice the contents of this guide, please consider attending Winmostar Introductory Training Session, Winmostar Basic Training Session, or Individual Training Session. (See page 2 for details.)
- If you are unable to proceed as instructed in this guide, please first consult Frequently asked questions.
- If FAQs do not resolve your issue, for the purposes of information accumulation and management, please contact us through Contact page, detailing the steps to reproduce the issue and attaching any generated files at that time.