

Development of experimental program for acquisition of equilibrium concept: from a standpoint of energy concept

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Abstract

An experimental program for acquisition of “equilibrium” concept was developed. The concept is one of chemical concepts classified into seven categories [1] of “atomic theory”, “chemical bond”, “oxidation and reduction”, “heat and energy”, “equilibrium”, “inorganic chemistry”, and “organic chemistry”.

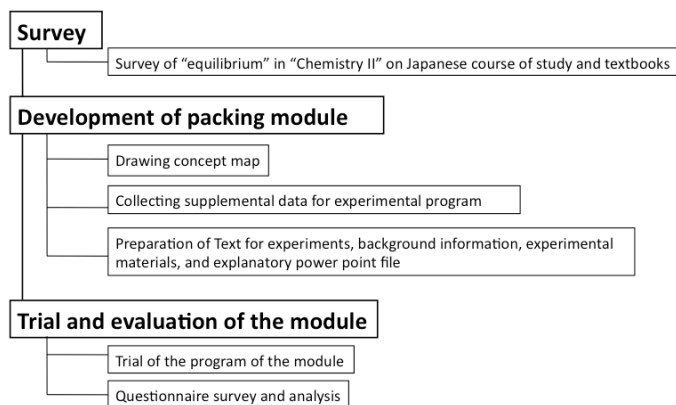
A survey of five present textbooks of “Chemistry II” on “equilibrium” in Japanese high school, which were compiled based on Japanese course of study (MEXT, 1999), was conducted. A packing module [2] type of experimental program of “equilibrium” was developed on the survey. The program was composed of text for experiments, experimental materials, background information, and explanatory power point file. The text was taken into consideration of insertion of numerous photographs in order that learner himself could do each experiment easily. Following concepts of lower rank on “thermodynamics” were chosen in the program by drawing the concept map; internal energy and Gibbs energy, liquid gas equilibrium, pressure change and temperature change. Targets of attainments on five steps were set in the program; color change, chemical reaction and color change in evaporation of Br₂ or equilibrium of N₂O₄ ⇌ 2NO₂, relationship between equilibrium and energy, measurements of the energy, and calculation of electron quantity from the energy by Daniel cell.

1. Introduction

Recently, a number of seminars for teacher are held to re-educate teachers in-service. It is important to develop experimental program for teacher education in which the program is consistent with a curriculum and applicable in wide range of institutions from elemental school to high school. In this paper, a packing module type [2] experimental program with a series of experiments related with equilibrium based on a survey of five present textbooks of “Chemistry II” on “equilibrium” in Japanese high school, which were compiled based on Japanese course of study (MEXT, 1999). The program includes three chemical concepts; thermodynamics, system, and external conditions. The program was developed for teacher of high school to grasp the concept of equilibrium through the experiments.

2. Development of the packing module

Scientific concepts and topics as a theme of the packing module was selected based on surveys Japanese course of study, textbooks [3] of “Chemistry II” currently used in Japanese high school, and textbook of general chemistry in the university. In order to contain all of experiments necessary to achieve the theme of the module, contents of the module is not restricted by the unit of high school textbook. Flow chart of development of the packing module is shown in Scheme1. Survey of “equilibrium” in “Chemistry II” on Japanese course of study and textbooks was conducted to select scientific theme and contents of the module. For development of packing module, concept map was drawn based on the survey. Supplemental data for experimental program was collected. Text for experiments, background information, experimental materials, and explanatory power point file were prepared.



Scheme 1. Flow of development of the packing module

Table 1. Policy for development of the packing module

1. The module is developed concerning scientific concepts and topics as a theme in the sequence from elementary school to college level.
2. The module is the experimental program for learner.
3. The module is adopted the type of a packing module which can complete in 3 hours.
4. The module is having the Text encouraging learner to do experiments themselves

Table 2. Composition of the packing module

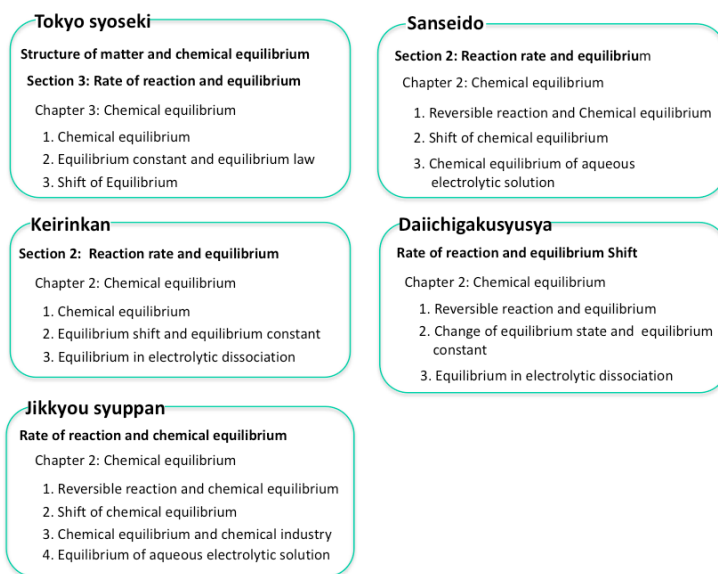
1. Module is composed of Text for experiments, experimental materials, explanatory power point file, and reference materials.
2. Text includes numerous photographs and schemes with artifice taking into account of easy access and simple thinking to a certain experiment nominated.
3. Module is compiled in order to the program proceeds smoothly in the following order; "explanation of adopted experiments", "exhibition of experiments by performer ", and "experiment by learners themselves"

Policy for development of the packing module is shown in Table 1. The module is developed concerning scientific concepts and topics as a theme in the sequence from elementary school to college level. The module is the experimental program for learner. The module is adopted the type of a packing module which can complete in 3 hours. The module is having the Text encouraging learners to do experiments themselves

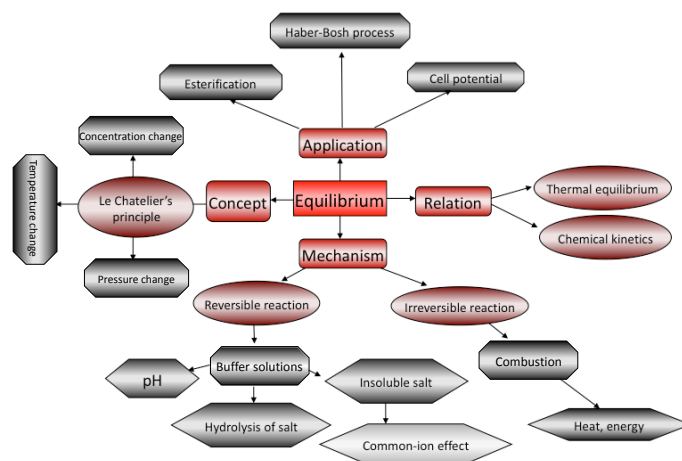
Composition of the packing module is shown in Table 2. The module is composed of Text for experiments, experimental materials, explanatory power point file, and reference materials. The Text includes numerous photographs and schemes with artifice taking into account of easy access and simple thinking to a certain experiment nominated. The module is compiled in order to the program proceeds smoothly in the following order; "explanation of adopted experiments", "exhibition of experiments by performer", and "experiment by learners themselves"

Survey of five most popular chemistry textbooks of “Chemistry II” currently used in Japanese high school (Textbooks, 2003, 2004), which were compiled based on Japanese course of study (MEXT, 1999), was conducted to investigate how “equilibrium” was described as in chemistry in the actual circumstances. Instruction items can be found in the table of contents in the textbooks. The items concerning about equilibrium in each textbooks is shown in

Scheme 2. Instruction items were mainly composed of chemical equilibrium, equilibrium constant, and equilibrium in electrolytic dissociation. Each textbook had a slight change of description. It is because all textbooks were compiled based on Japanese course of study (MEXT, 1999), which stated that “Chemical equilibrium” is introduced in the chapter of “(1) Structure of matter and chemical equilibrium” and “Introduction of equilibrium constant is limited to simple system of weak acid and weak base.”, “Ion product for water is introduced.”, and “Shift of equilibrium is introduced



Scheme 2. Index concerning about equilibrium in text books of high school chemistry



Scheme 3. Concept map of equilibrium within study of high school chemistry

mainly Le Chatelier's principle."

In order to see relationship between the theme of the module and concepts or topics, concept map of equilibrium within study of high school was drawn. The concept map is shown in Scheme 3. In the concept map, concept was mainly related to Le Chatelier's principle as described before.

Other relations were among thermal equilibrium and chemical kinetics. Reaction mechanisms were related to reversible and irreversible reactions. Applications of equilibrium were described such as esterification, Harber-Bosh process, and cell potential.

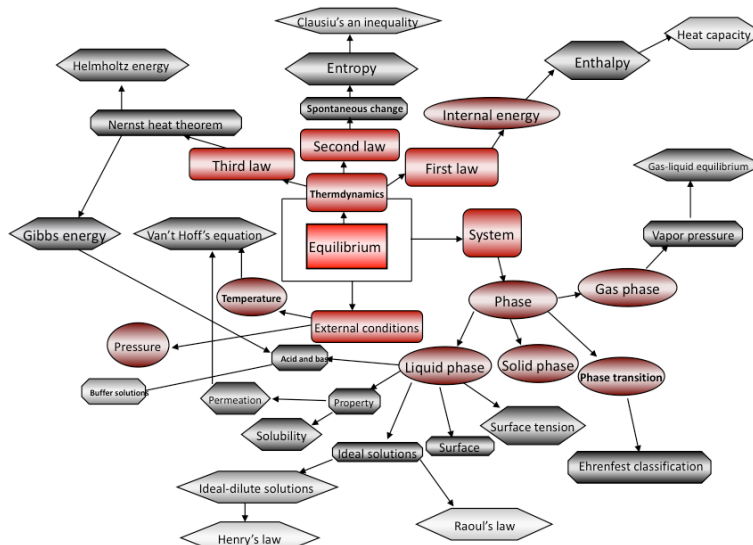
Concept map of equilibrium was extended to the study of general chemistry in the university. The concept map is shown in Scheme 4.

For quantitative handling of equilibrium, concept of

thermodynamics including the first law to the third law was introduced in the university.

Related concepts such as system and external conditions were also introduced. Those concepts were further related to internal energy, enthalpy, entropy, and Gibbs energy and so on. Following concepts of lower rank on "thermodynamics" were chosen in the module; internal energy and Gibbs energy, liquid gas equilibrium, pressure change and temperature change.

Targets of attainments on five steps were set in the module. Steps and contents of



Scheme 4. Concept map of equilibrium within study of general chemistry in university

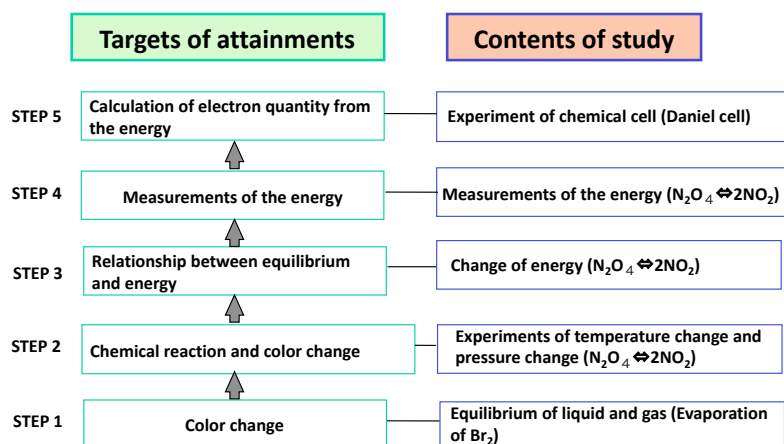


Figure 1. Steps and contents of experimental program

experimental program are shown in Figure 1. Qualitative observation of simple experiment such as color change of bromine vapor in different temperatures was introduced in the step 1. Color change due to chemical reaction such as temperature change and pressure change of dinitrogen tetraoxide and nitrogen dioxide mixture ($\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$) was introduced in the step 2. Relationship between equilibrium and energy such as drawing of figure of equilibrium constant vs. concentration of N_2O_4 was introduced in the step 3. Measurements of the energy such as calculation of Gibb's energy of N_2O_4 and NO_2 system were introduced in the step 4. Calculation of electron quantity from the energy of Daniel cell was introduced in the step 5. Program included qualitative observation of color change in evaporation of Br_2 to quantitative calculation of electron in Daniel cell in order to grasp the concept of equilibrium from a standpoint of energy concept.


3. Experimental program

Abridgment of page 1 of the text from appendix 1 is shown in Figure 2. In the section I, gas-liquid equilibrium of bromine, learners observe color of bromine vapor in different temperatures such as 20, 40 and 0.5 °C. Learner is asked to sketch the color of bromine vapor in the corresponding figure of the text, and is asked to take a note to compare the color of bromine vapor in room temperature (20 °C), in hot water (40 °C), and in ice-bath (0.5 °C), in the corresponding area of the text. Equilibrium of liquid and gas was studied by qualitative observation of color change of evaporation bromine in different temperatures. The text was taken into consideration of insertion of numerous photographs in order that learner himself could do each experiment easily.

化学平衡


I Br_2 (気液平衡) (演示)

実験 臭素の温度変化



i) 封管した臭素
室温 (20°C)

➡



A (40 °C) B (0.5 °C)
(観察・図示する)

ii) 湯(40°C), 氷水(0.5°C)に入れる


結果 温度により色はどう変化したか?

Br_2	A	B
室温との比較		

II $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ (温度変化と圧力変化) (演示)


i) 温度変化

実験 温度を変えるとどのように変化するか?



i) 封管した N_2O_4

➡



A (80 °C) B (0.5 °C)
(観察・図示する)

ii) 湯(80°C), 氷水(0.5°C)に入れる

材料

- ・臭素
- ・純正一級
- CAS No. 7726-95-6
- ・純正化学株式会社
- ・湯 (40°C)
- ・氷水

使用器具

- ・ビーカー (500mL × 3)
- ・ガラス管 (直径 15mm)
- ・ガスバーナー
- ・ガラスカッター

臭素の物性

Br: 原子番号35,
原子量79.916
室温で揮発臭の強い赤褐色の高気圧を放つ。
融点-7.2°C,
沸点58.8°C,
出版: 化学大辞典より

材料

- ・濃硝酸
- ・試薬特級
- Assay: 95~98%
- ・和洋純工業株式会社
- ・銅片 (3~5片)
- ・氷水
- ・湯 (80°C)

使用器具

- ・二液試験管
- ・誘導管
- ・ガラス管 × 2
- ・シリコン (50 mL)
- ・ビーカー (500 mL × 3)
- ・ゴム栓 × 1

Figure 2 Abridgment of page 1 of the Text

Properties of chemicals used in the experiment were described in the right side of the page along with description where they were purchased. In this way learner can study by himself after the class.

Abridgment of page 4 of the text from appendix 4 is shown in Figure 3. In the section IV, the measurements of the energy, learners are asked to calculate Gibb's free energy by use of data provided in the right side of the text. In the section of V Calculation of electron quantity from the experiment of chemical cell, learners measure potential of Daniel cell and also calculate free energy change. Learner is also asked to calculate quantity of electron.

IV エネルギーの定量 (ドライラボ)

$N_2O_4 = 2NO_2$ $-\Delta G$

$2\Delta G_1, NO_2$ $-\Delta G_2, N_2O_4 =$ _____ kJmol^{-1}

	$\Delta G_f / \text{kJ mol}^{-1}$
$NO_2(g)$	-51.31
$N_2O_4(g)$	-97.89
$N(g)$	455.56
$N_2(g)$	0
$O(g)$	231.73
$O_2(g)$	0

ΔG_f : 標準生成ギブズエネルギー
化学便覧, 基礎編Ⅱ, 改訂4版
(1993), 日本化学会編, 丸善

V ダニエル電池実験による電子の定量 (実験、各テーブル)

i) 起電力の極板依存

ii) 起電力の極板依存

1) 硫酸銅(II)飽和水溶液及び4%の硫酸亜鉛(II)水溶液を調製する。

ii) 負極槽と正極槽に硫酸銅(II)飽和水溶液と硫酸亜鉛(II)水溶液をそれぞれ加え、負極に亜鉛板、正極に銅板を浸す。

iii) 電圧計を並列につないで電流、電圧の値を測定する。

両極板が電解液に浸る面積 / cm^2	電圧 / V
2	(1) _____
4	(2) _____

エネルギー図

材料
・硫酸亜鉛(II)七水和物 試薬特級 和光純薬工業株式会社製
・硫酸銅(II)五水和物 試薬特級 和光純薬工業株式会社製
・蒸留水

使用器具
電池キット
ポルタダニエル電池
VD No. 123-045. (株)ケニス製

Figure 3 Abridgment of page 4 of the Text

4. Conclusion

A survey of present textbooks in Japanese high school indicated that instruction items were mainly composed of chemical equilibrium, equilibrium constant, and equilibrium in electrolytic dissociation. A packing module type of experimental program of “equilibrium” was developed on the survey. Program included qualitative observation of color change in evaporation of Br_2 to quantitative calculation of electron in Daniel cell in order to grasp the concept of equilibrium from a standpoint of energy concept. The program could be applied for teachers in-service.

Reference

- [1] OGAWA, H., OKADA, S., TAKEHARA, Y., and IKUO, A., Bull. Tokyo Gakugei Univ., 58, 95-106 (2006) (in Japanese).
- [2] Akira IKUO, Yusuke YOSHINAGA, Haruo OGAWA, J. Sci. Educ. Japan, 32, 39-55 (2008) (in Japanese).
- [3] Textbooks of “Chemistry II” in Japanese high school: a) Daiichigakusyusya (2004); b) Jikkyosyuppan (2004); c) Keirinkan (2003); d) Sanseido (2004); e) Tokyosyoseki

(2004) (all in Japanese). Textbooks were listed in alphabetical order.

Appendix 1. Page 1 of the Text


化学平衡

(東京学芸大学教育学部) 小川治雄, 吉永裕介, 生尾光


I Br_2 (気液平衡) (演示)

実験 臭素の温度変化

i) 封管した臭素
室温 (20°C)



ii) 湯(40°C), 氷水(0.5°C)に入れる



A (40 °C) B (0.5°C)
(観察・図示する)

結果 温度により色はどう変化したか?

Br_2	A	B
室温との比較		

II $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ (温度変化と圧力変化) (演示)

i) 温度変化

実験 温度を変えるとどのように変化するか?

i) 封管した NO_2



ii) 湯(80°C), 氷水(0.5°C)に入れる



A (80 °C) B (0.5°C)
(観察・図示する)

観察(A条件)

観察(B条件)

材料

- ・臭素
純正一級
CAS No. 7726-95-6
純正化学株式会社
- ・湯 (40°C)
- ・氷水

使用器具

- ・ビーカー (500mL × 3)
- ・ガラス管 (直径 15mm)
- ・ガスバーナー
- ・ガラスカッター

臭素の物性

Br. 原子番号35.
原子量79.916.
室温で刺激臭の強い赤褐色の蒸気を放つ。
融点-7.2°C.
沸点58.8°C.
出展：化学大辞典より

材料

- ・濃硝酸
試薬特級
Assay 65~66%
和光純薬工業株式会社
- ・銅片 (3~5片)
- ・氷水
- ・湯 (80°C)

使用器具

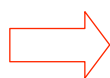
- ・二股試験管
- ・誘導管
- ・ガラス管 × 2
- ・シリンジ (50 mL)
- ・ビーカー (500 mL × 3)
- ・ゴム栓 × 1

ii) 圧力変化

実験 圧力を変えるとどのように変化するか？



i) 常圧で NO_2 を 10mL 入れる。



ii) 注射器のピストンを 50mL まで上げる。
(圧力 1/5 倍)

観察



iii) 注射器のピストンを 5mL まで下げる。
(圧力 2 倍)

観察



iv) ii) から 1 分後

観察



v) iii) から 1 分後

観察

観察のまとめ

注射器を縦(ピストン)方向から見ると観察が容易との提案がなされている。

下田義夫・高江洲敏・富岡康夫, 化学と教育, 36(6), pp. 618-621 (1988).

栗岡誠次, 化学と教育, 47(8), p. 574 (1999)

Ⅲ. $N_2O_4 \rightleftharpoons 2NO_2$ (濃度変化と平衡定数) (ドライラボ)

i) K_c の平均値より ΔG を求める。

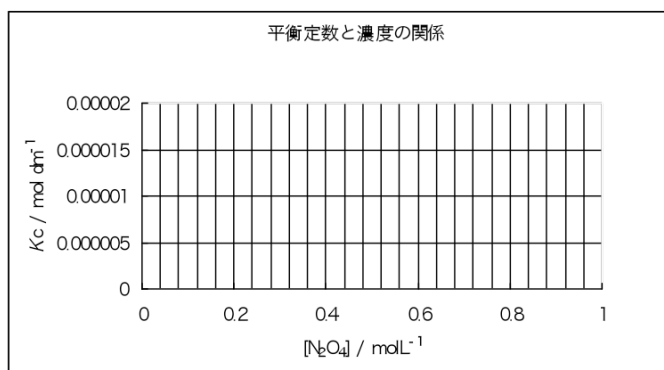
$$\frac{(1)+(2)+(3)+(4)}{4} = (5) \text{ mol L}^{-1}$$



$$\Delta G = -8.31447 \text{ JK}^{-1} \text{ mol}^{-1} \times (273+25) \text{ K} \times \ln(5) = (6) \text{ J mol}^{-1}$$

ii) グラフより ΔG を求める。

$[N_2O_4]$ のグラフを書く (PC)。Table のデータを使用する。



$$K_c = (7) \text{ mol L}^{-1}$$

$$\Delta G = -8.31447 \text{ J K}^{-1} \text{ mol}^{-1} \times (273+25) \text{ K} \times \ln(7) = (8) \text{ J mol}^{-1}$$

(6) と (8) の差の比較

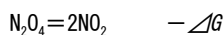
$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Table

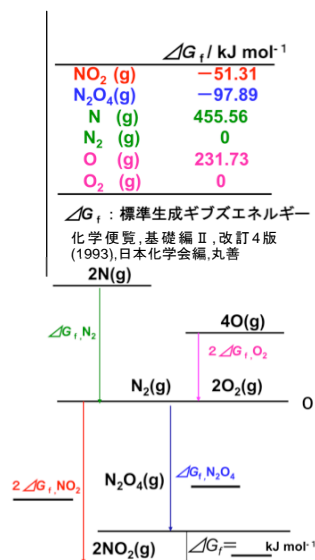
$[N_2O_4] / \text{mol L}^{-1}$	K_c
0.780	(1) 1.38×10^{-5}
0.406	(2) 1.50×10^{-5}
0.260	(3) 1.47×10^{-5}
0.129	(4) 1.42×10^{-5}

(化学便覧 基礎編Ⅱ 改訂Ⅱ
版 日本化学会編 丸善)

IV エネルギーの定量 (ドライラボ)



$$2\Delta G_f, \text{NO}_2 \quad -\Delta G_f, \text{N}_2\text{O}_4 = \underline{\hspace{2cm}} \text{kJmol}^{-1}$$



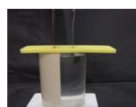
エネルギー図

V ダニエル電池実験による電子の定量 (実験、各テーブル)

i) 起電力の極板依存



i) 硫酸銅(II)飽和水溶液及び4wt%の硫酸亜鉛(II)水溶液を調製する。



ii) 負極槽と正極槽に硫酸銅(II)飽和水溶液と硫酸亜鉛(II)水溶液をそれぞれ加え、負極に亜鉛板, 正極に銅板を浸す。



iii) 電圧計を並列につないで電流, 電圧の値を測定する。

両極板が電解液に浸る面積 / cm^2	電圧 / V
2	(1) <u> </u>
4	(2) <u> </u>
6	(3) <u> </u>
8	(4) <u> </u>
10	(5) <u> </u>

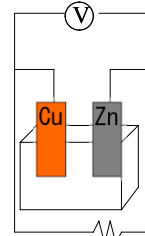
$$\frac{(1) + (2) + (3) + (4) + (5)}{5} = (6) \underline{\hspace{2cm}} \text{V}$$

材料

- ・硫酸亜鉛(II)七水和物 試薬特級 和光純薬工業株式会社製
- ・硫酸銅(II)五水和物 試薬特級 和光純薬工業株式会社製
- ・蒸留水

使用器具

- 電池キット
- ボルタ・ダニエル電池
- VD. No. 123-045, (株)ケニス製



ダニエル電池 回路

平均電圧 = (6) _____ V

ii) 起電力と ΔG の関係

起電力 (6) から電池反応における自由エネルギー変化量 ΔG を求める。

$$\Delta G = -nFE = -nL_A E = -2 \times 1.602 \times 10^{-19} \text{C} \times 6.022 \times 10^{23} \text{mol}^{-1} \times (6)$$

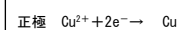
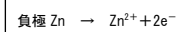
$$= (7) \text{ Jmol}^{-1}$$

iii) 起電力と反応が 1 モル分起こるときの電子の個数

$$\text{動く電子数} = 2 \text{ モル分}$$

$$\text{電子個数} = n \cdot L_A = 2 \text{mol} \times 6.022 \times 10^{23} \text{ mol}^{-1} = (8) \text{ コ}$$

ダニエル電池半反応式



電池の起電力の式

$$-\Delta G = nFE$$

ΔG : 標準ギブズエネルギー

n : 電子の個数

E : 起電力

F : ファラデー定数

* $F = \text{電子 1 個の価数} \times$

アボガドロ数

$e: 1.602 \times 10^{-19} \text{ C}$

$L_A: 6.02 \times 10^{23} \text{ mol}^{-1}$