Physical Chemistry for Energy Engineering (1st: 2018/09/03)

Takuji Oda

Associate Professor, Department of Nuclear Engineering
Seoul National University

*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Contents of today

1. What is Physical Chemistry?
2. Physical Chemistry in Nuclear Engineering
3. Outline of this course
4. Short introduction of topics

Goals of today's lecture
- ✓ Understand what is Physical Chemistry.
- ✓ Understand what we are going to learn in this course.

[Instructor]
Assoc. Prof. Takuji Oda (oda@snu.ac.kr) @32-218 room.
[Assistance Instructor]
Mr. 이현석 (falconv@snu.ac.kr)

Physical Chemistry?

- ✓ **Physical chemistry** is the study of macroscopic, atomic, subatomic, and particulate phenomena in chemical systems in terms of laws and concepts of physics. It applies the principles, practices and concepts of physics such as motion, energy, force, time, thermodynamics, quantum physics, statistical mechanics and dynamics, equilibrium.
  - "Physics (classical/quantum mechanics/dynamics)"
  - "Thermodynamics"
  - "Statistical mechanics/dynamics"
  - "Equilibrium"

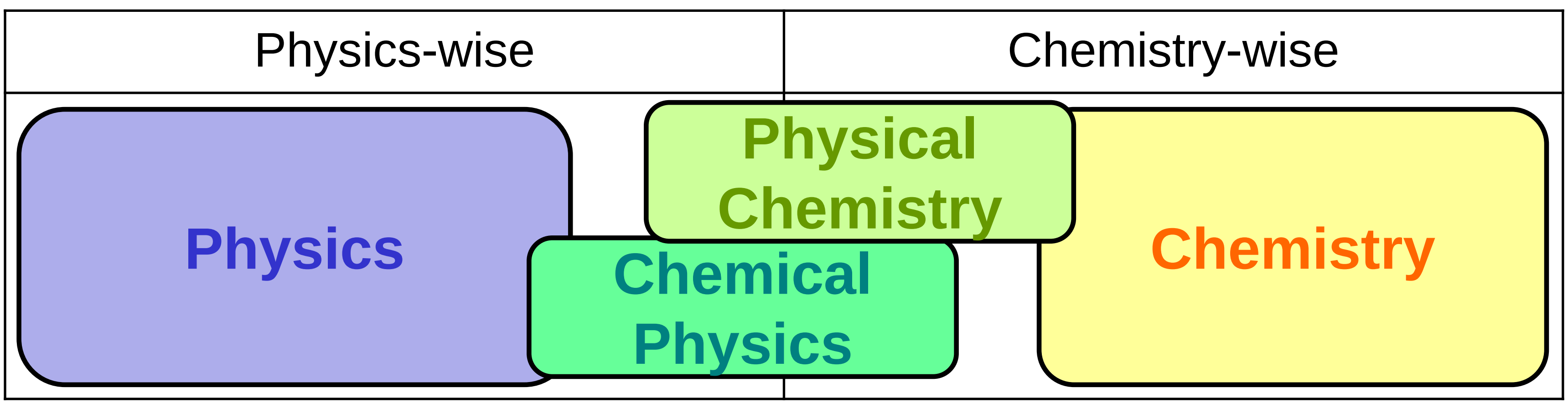
- ✓ **Physical chemistry**, in contrast to chemical physics, is predominantly (but not always) a macroscopic or supra-molecular science, as the majority of the principles on which physical chemistry was founded, are concepts related to the bulk rather than on molecular/atomic structure alone. For example, chemical equilibrium,……

*wikipedia

Chemical physics?

✓ **Chemical physics** is a sub-discipline of chemistry and physics that investigates physicochemical phenomena using techniques from atomic and molecular physics and condensed matter physics; it is the branch of physics that studies chemical processes from the point of view of physics. While at the interface of physics and chemistry, chemical physics is distinct from physical chemistry in that it focuses more on the characteristic elements and theories of physics. Meanwhile, physical chemistry studies the physical nature of chemistry. Nonetheless, the distinction between the two fields is vague, and workers often practice in each field during the course of their research.

*wikipedia



e.g.) Related scientific journals

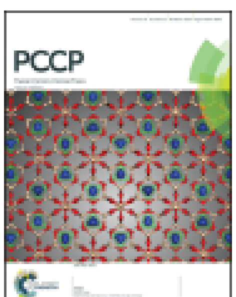
<American Chemical Society(ACS)>

THE JOURNAL OF PHYSICAL CHEMISTRY A

<American Institute of Physics (AIP)>

AIP | The Journal of Chemical Physics

<Royal Society of Chemistry (RSC)>



Physical Chemistry Chemical Physics

High quality research in physical chemistry, chemical physics and biophysical chemistry.

Impact Factor 3.829 | 48 Issues per Year | Indexed in MEDLINE

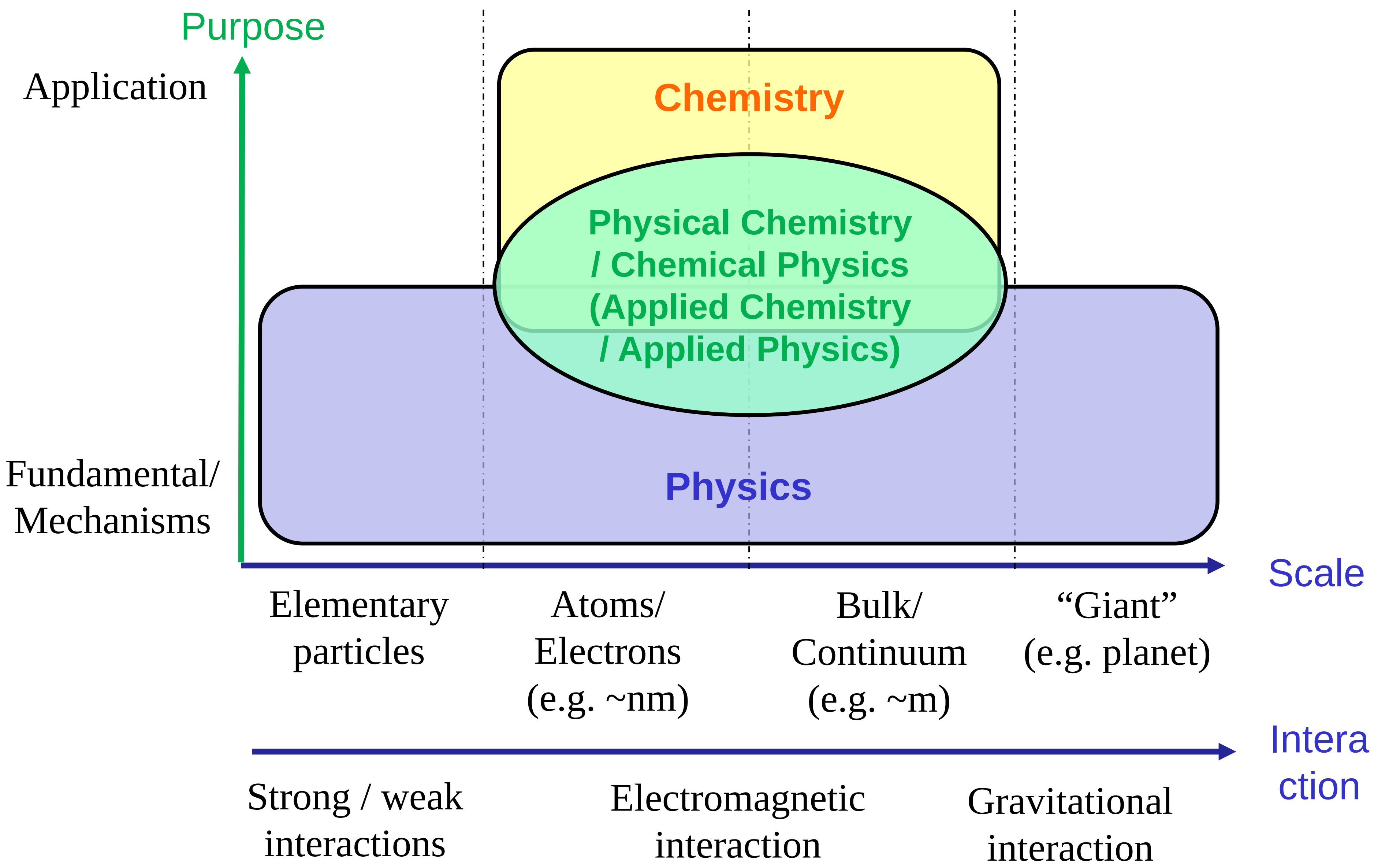
Chemistry? Physics?

- ✓ **Chemistry,** a branch of physical science, is the study of the composition, properties and behavior of matter. As it is a fundamental component of matter, the atom is the basic unit of chemistry. Chemistry is concerned with atoms and their interactions with other atoms, with particular focus on the properties of the chemical bonds formed between species. Chemistry is also concerned with the interactions between atoms or molecules and various forms of energy (e.g. photochemical reactions, oxidation-reduction reactions, changes in phases of matter, …, etc.).

- ✓ **Physics** is the natural science that involves the study of matter and its motion through space and time, along with related concepts such as energy and force. More broadly, it is the general analysis of nature, conducted in order to understand how the universe behaves.

*wikipedia

What is Physical Chemistry?



Subjects in Physical Chemistry

Some of the relationships that physical chemistry strives to resolve include the effects of:

1. Intermolecular forces that act upon the physical properties of materials (plasticity, tensile strength, surface tension in liquids). (solid state physics/mechanics)
2. Reaction kinetics on the rate of a reaction. (rate theory, kinetics)
3. The identity of ions and the electrical conductivity of materials. (e.g. diffusion theory)
4. Surface chemistry and electrochemistry of membranes.
5. Interaction of one body with another in terms of quantities of heat and work called thermodynamics.
6. Transfer of heat between a chemical system and its surroundings during change of phase or chemical reaction taking place called thermochemistry.
7. Number of phases, number of components and degree of freedom (or variance) can be correlated with one another with help of phase rule. (e.g. phase equilibrium)
8. Reactions of electrochemical cells. (electrochemistry)

*wikipedia

Contents of today

1. What is Physical Chemistry?

2. Physical Chemistry in Nuclear Engineering

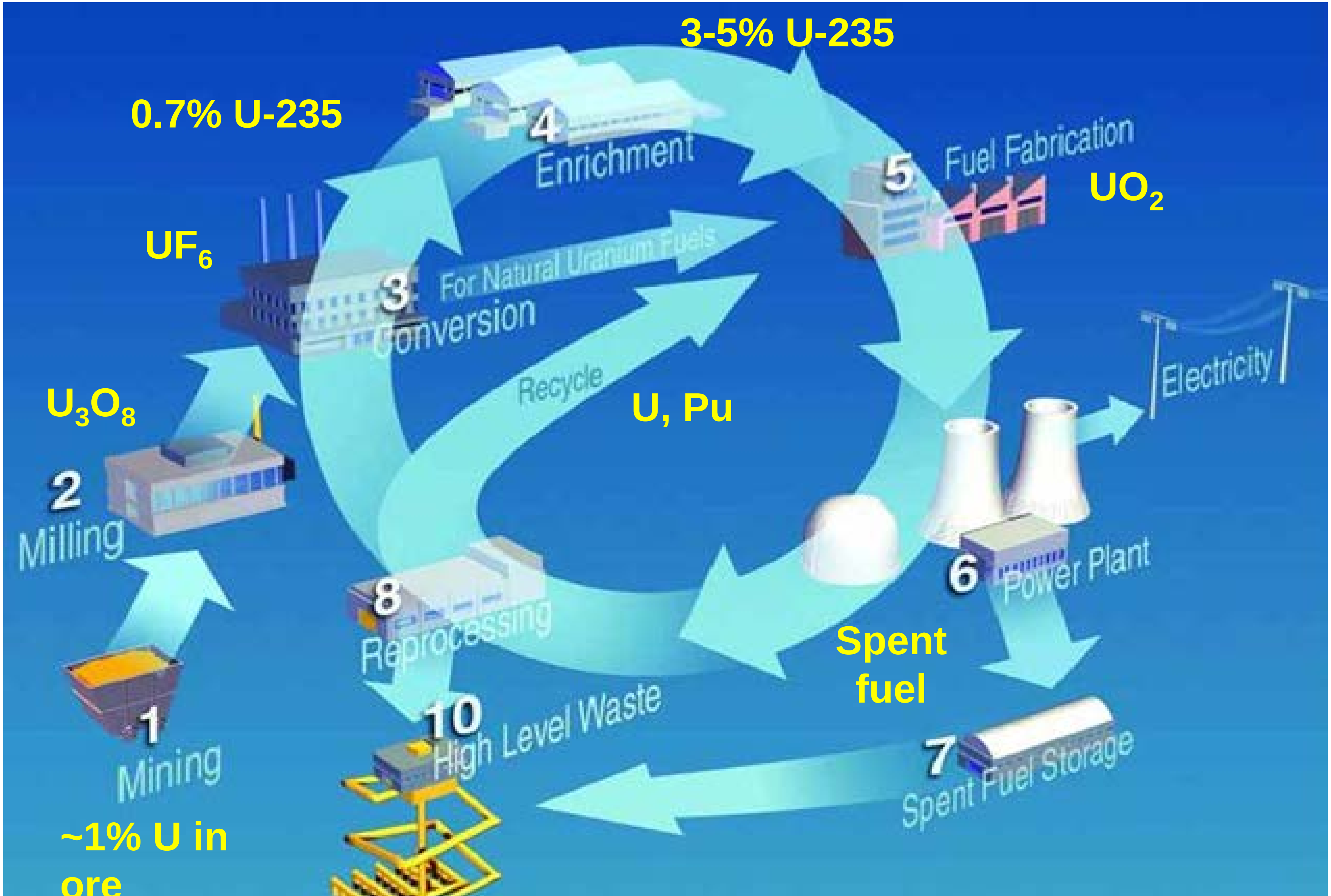
3. Outline of this course

4. Short introduction of topics

Goals of today’s lecture

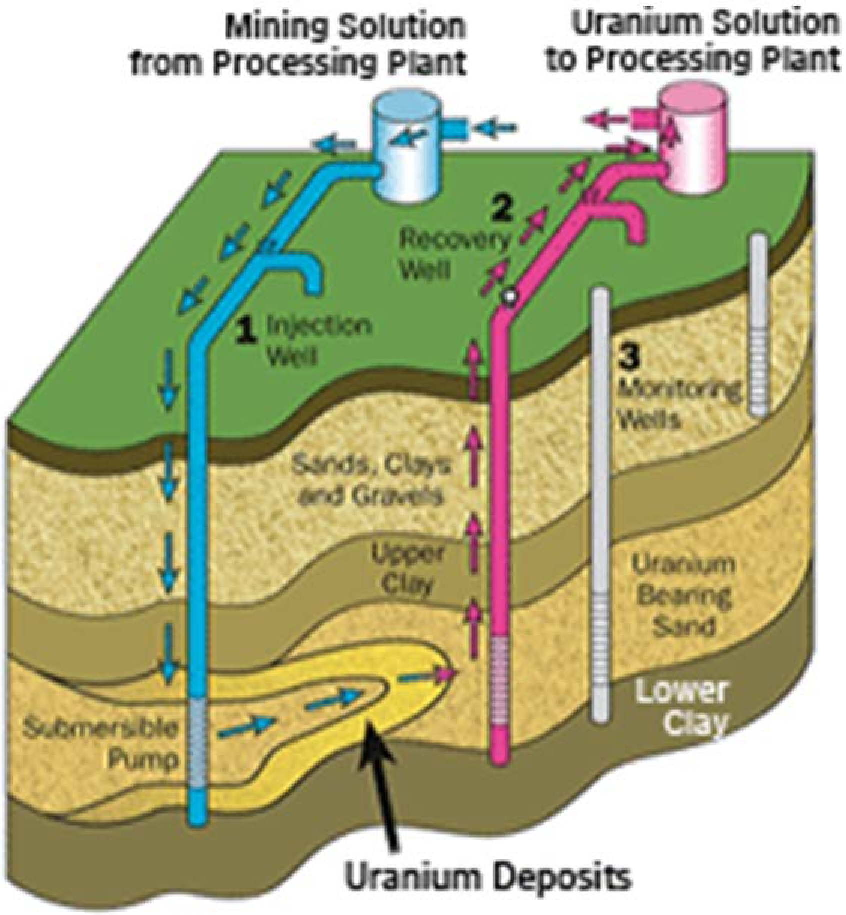
- ✓ Understand what is Physical Chemistry.
- ✓ Understand what we are going to learn in this course.

An example: fuel cycle



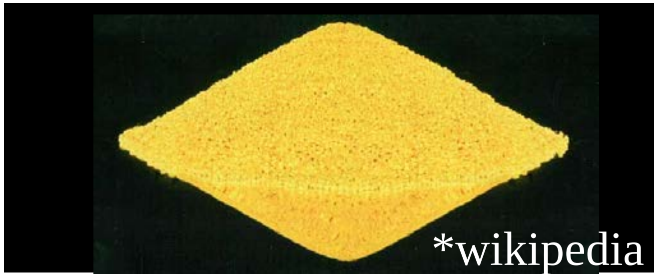
*IAEA (cycle figure); wikipedia (pictures)

Mining by "in-situ leach (ISL)"

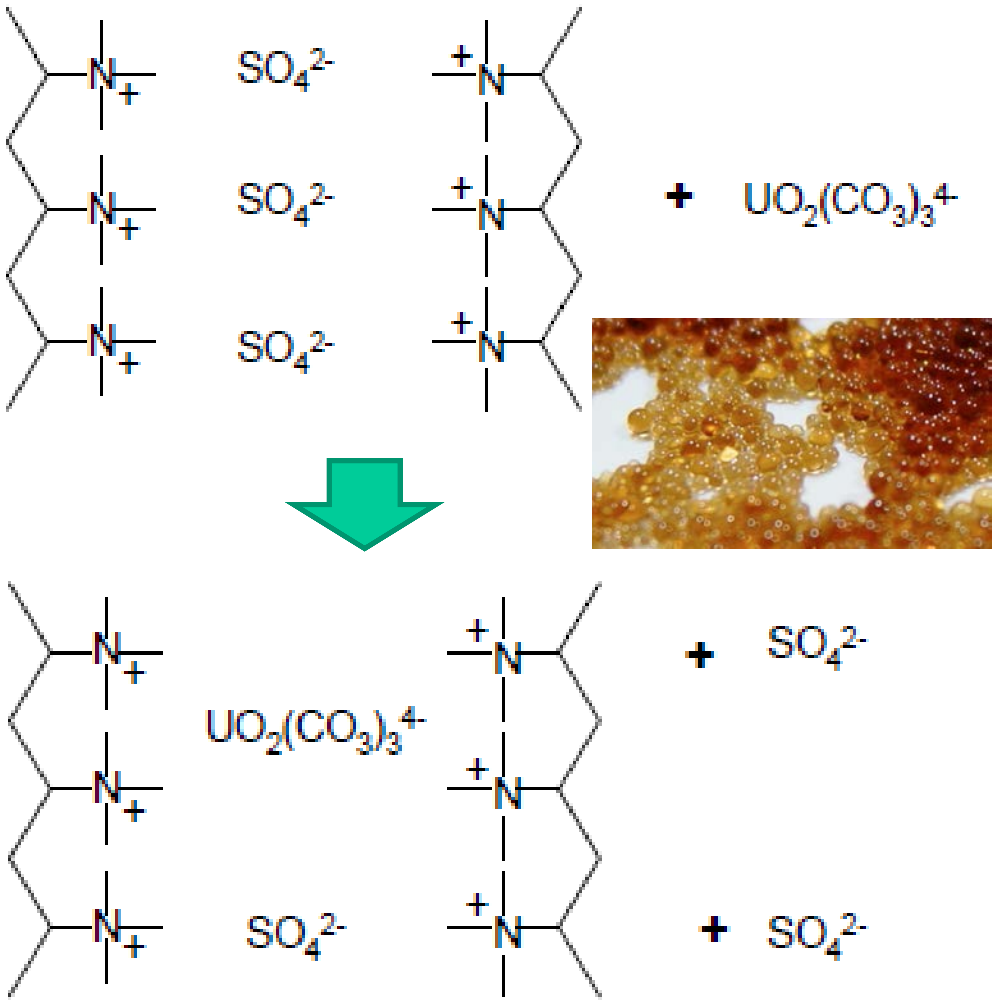


*http://www.nrc.gov/materials/uranium-recovery/extraction-methods/isl-recovery-facilities.html

1. A solution (typically containing water mixed with oxygen and/or hydrogen peroxide) is injected through a series of wells into the ore body to dissolve the uranium.
2. The solution is then collected in a series of recovery wells. Then, the uranium is extracted from the solution through an ion-exchange process.
3. The uranium extract is then further purified, concentrated, and dried to produce a material ("yellowcake"; mostly U_3O_8)



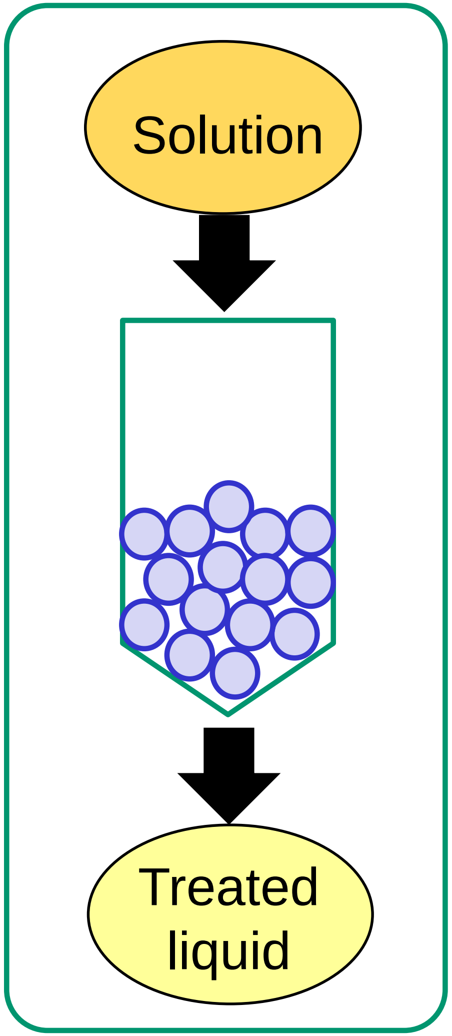
Extracting Uranium by ion exchange

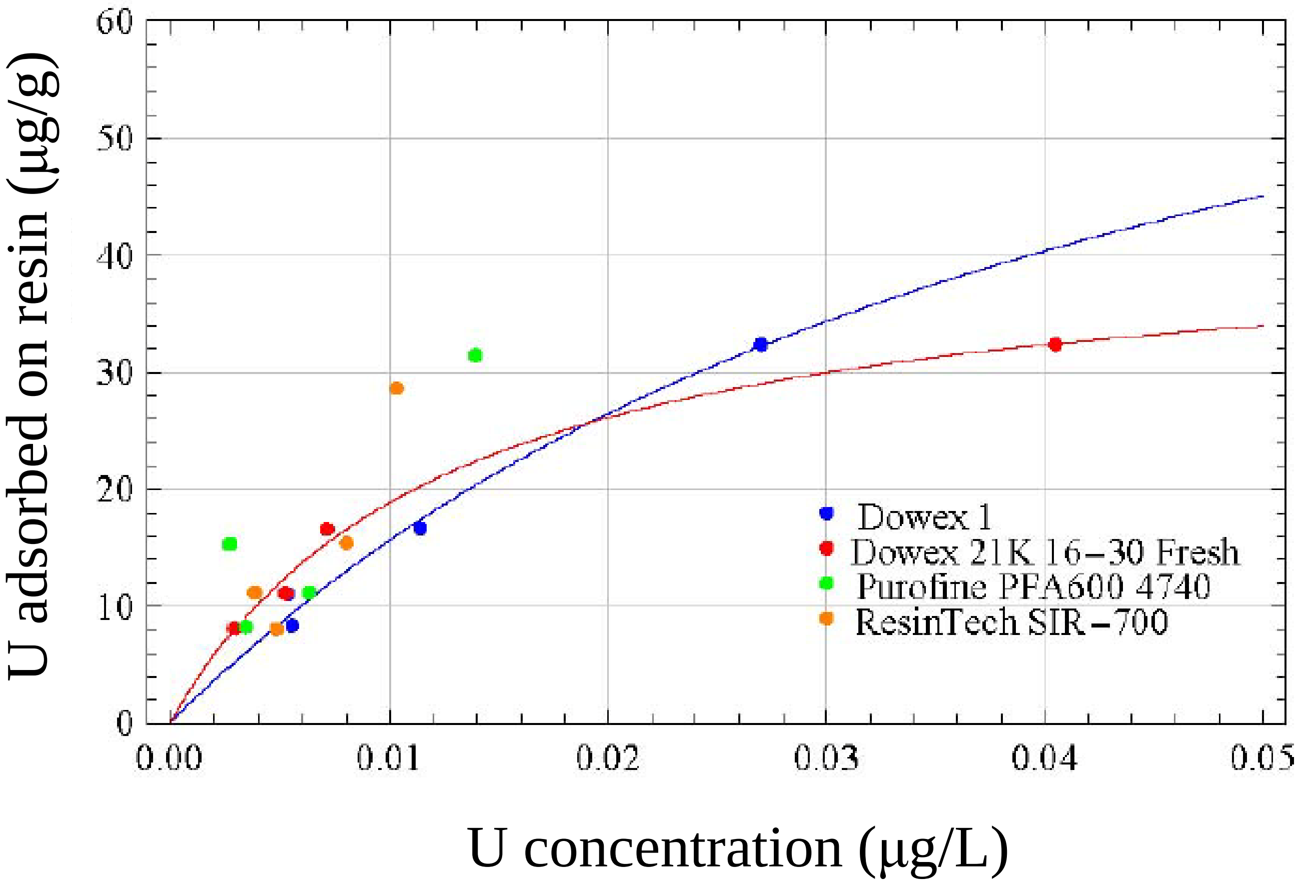


*M. BOTHA et al., INWA-2009.
*wikipedia (resin picture)

- ✓ "How much U can be caught by resin" may be determined by chemistry.
- ✓ "How resin catch U" may be determined by physical chemistry based on equilibrium theory, rate theory and quantum mechanics.

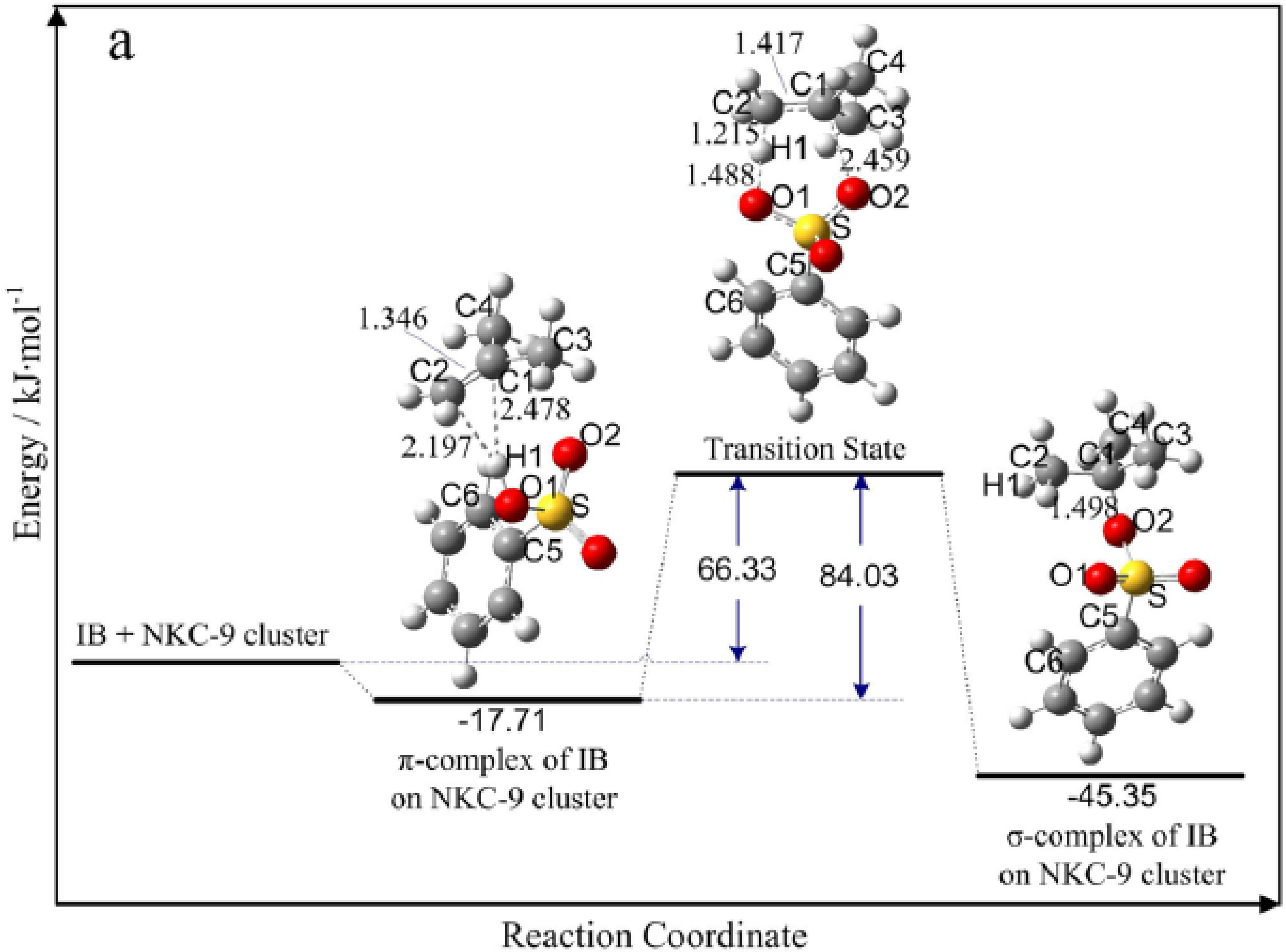
Approach-1) Chemical experiment





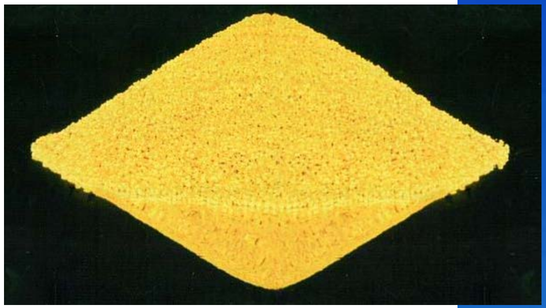
*http://www.pnl.gov/main/publications/external/technical_reports/PNNL-20135.pdf

Approach-2) Rate-theoretical approach combined with quantum mechanics



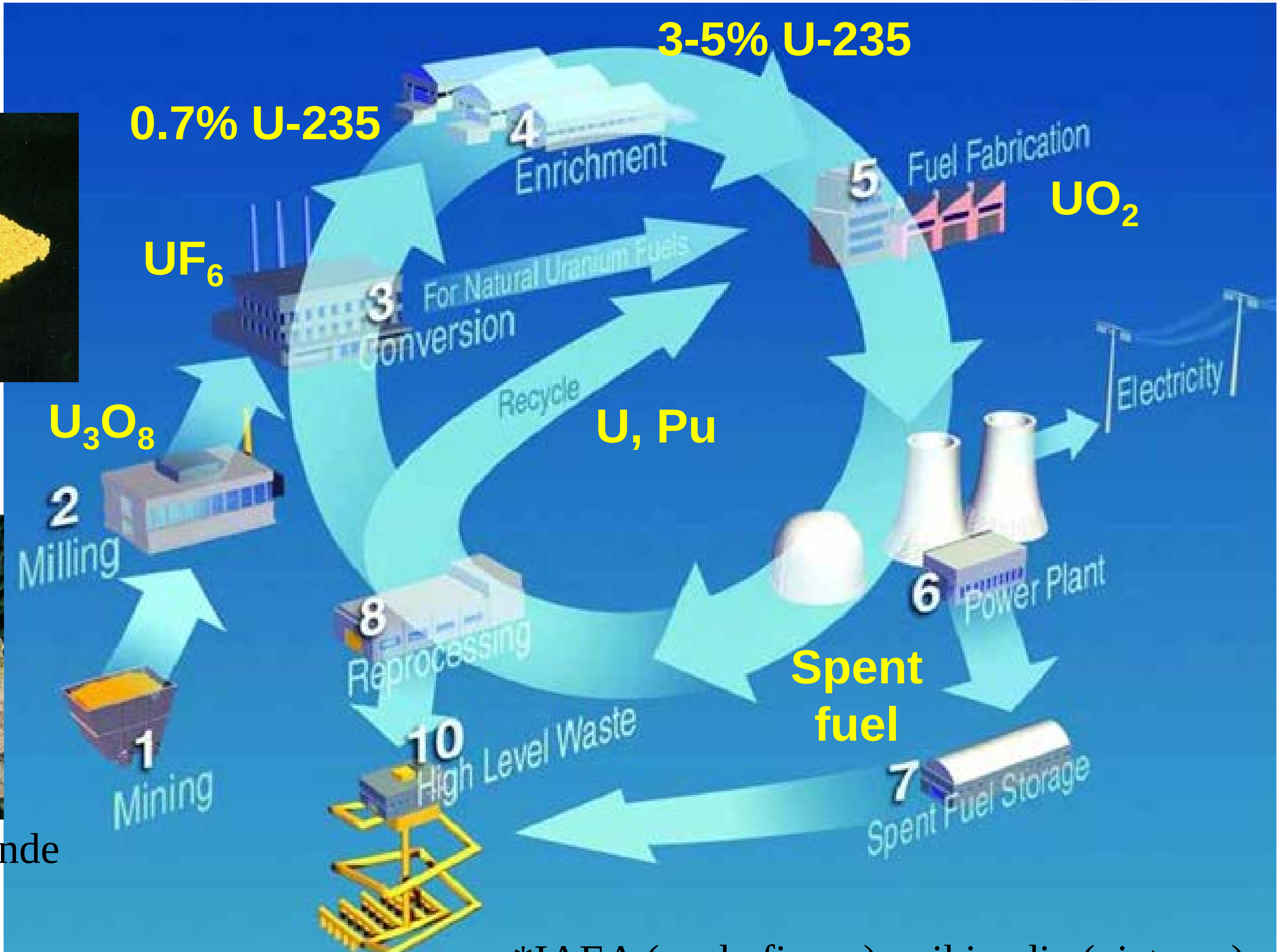
Y. Liu et al., Ind. Eng. Chem. Res., **2013**, *52* (21), pp 6933–6940.

Nuclear Fuel Cycle -focusing on fuel-



* “Yellowcake” (U_3O_8)

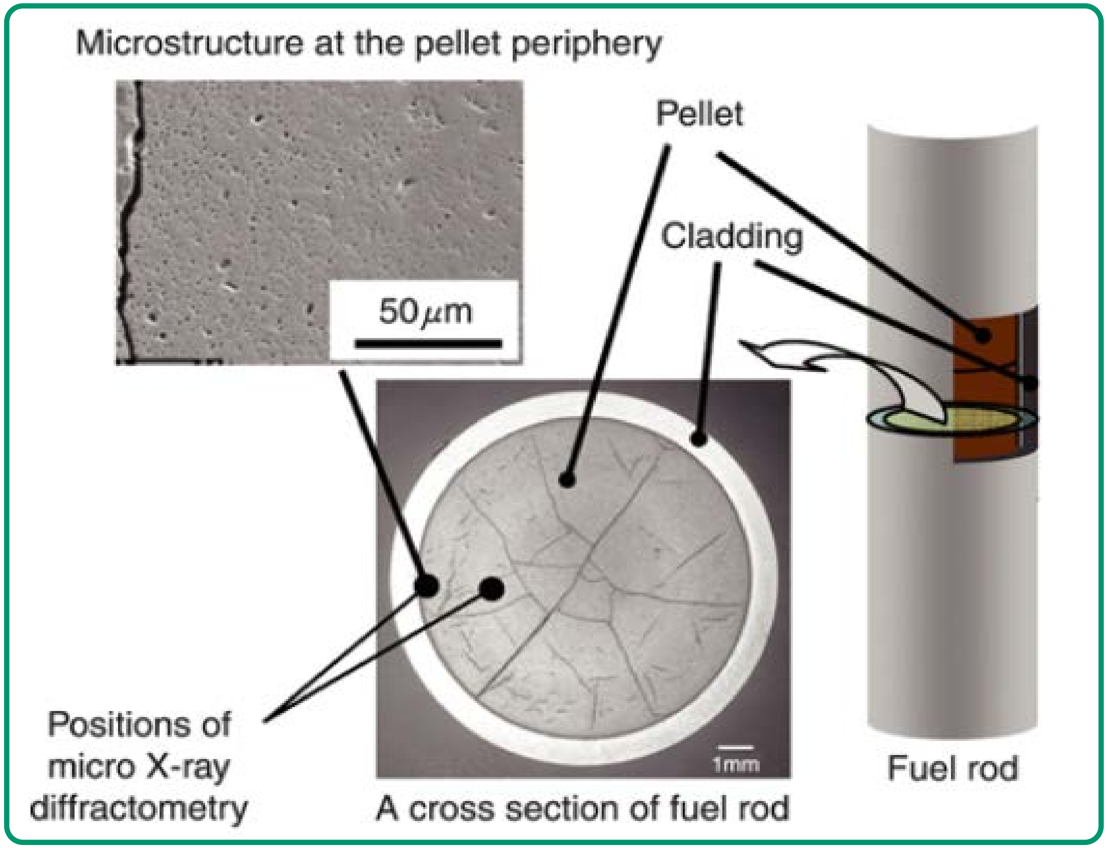
*Uranium ore (pitchblende [black]; mainly U_3O_8)

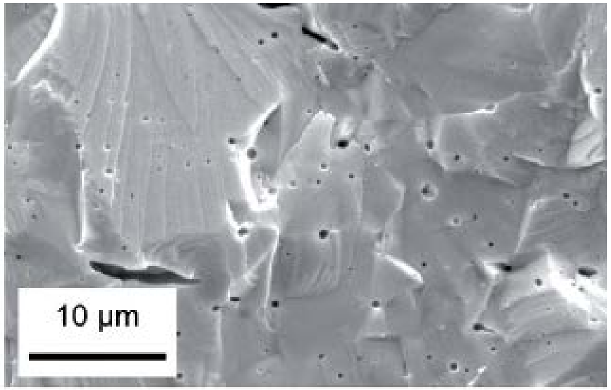


*IAEA (cycle figure); wikipedia (pictures)

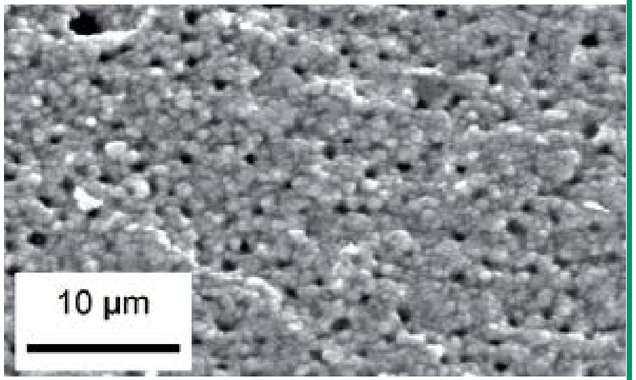
Typical nuclear-engineering topics
- What happens after irradiation?-

After irradiation





After ~75 GWd/tHM

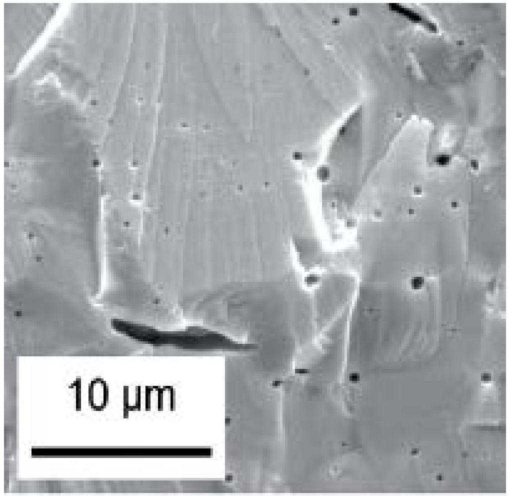


*http://jolisfukyu.tokai-sc.jaea.go.jp/fukyu/mirai-en/2009/5_3.html

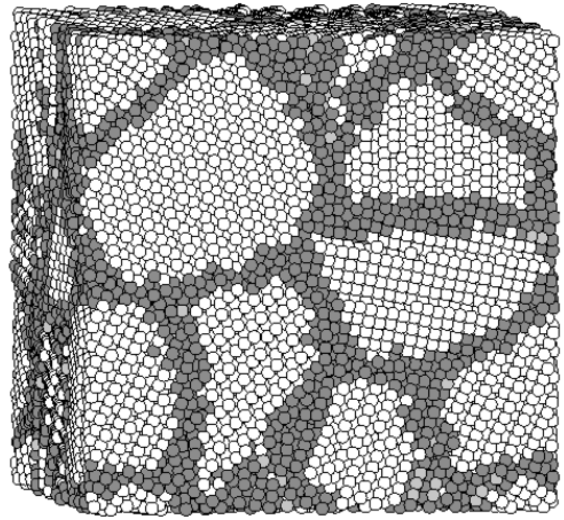
*http://in.mse.drexel.edu/blogs/nuclear/attachment/9005.ashx

These topics are covered in other courses, such as “Introduction to nuclear materials” and some graduate course.

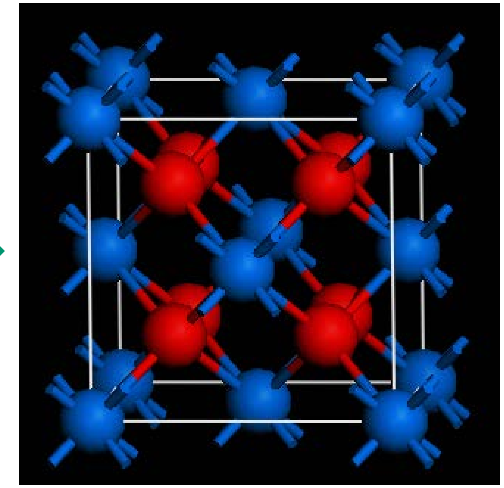
Multi-scape characteristics of materials



~20 µm



~20 nm



~0.5 nm

Thermodynamics

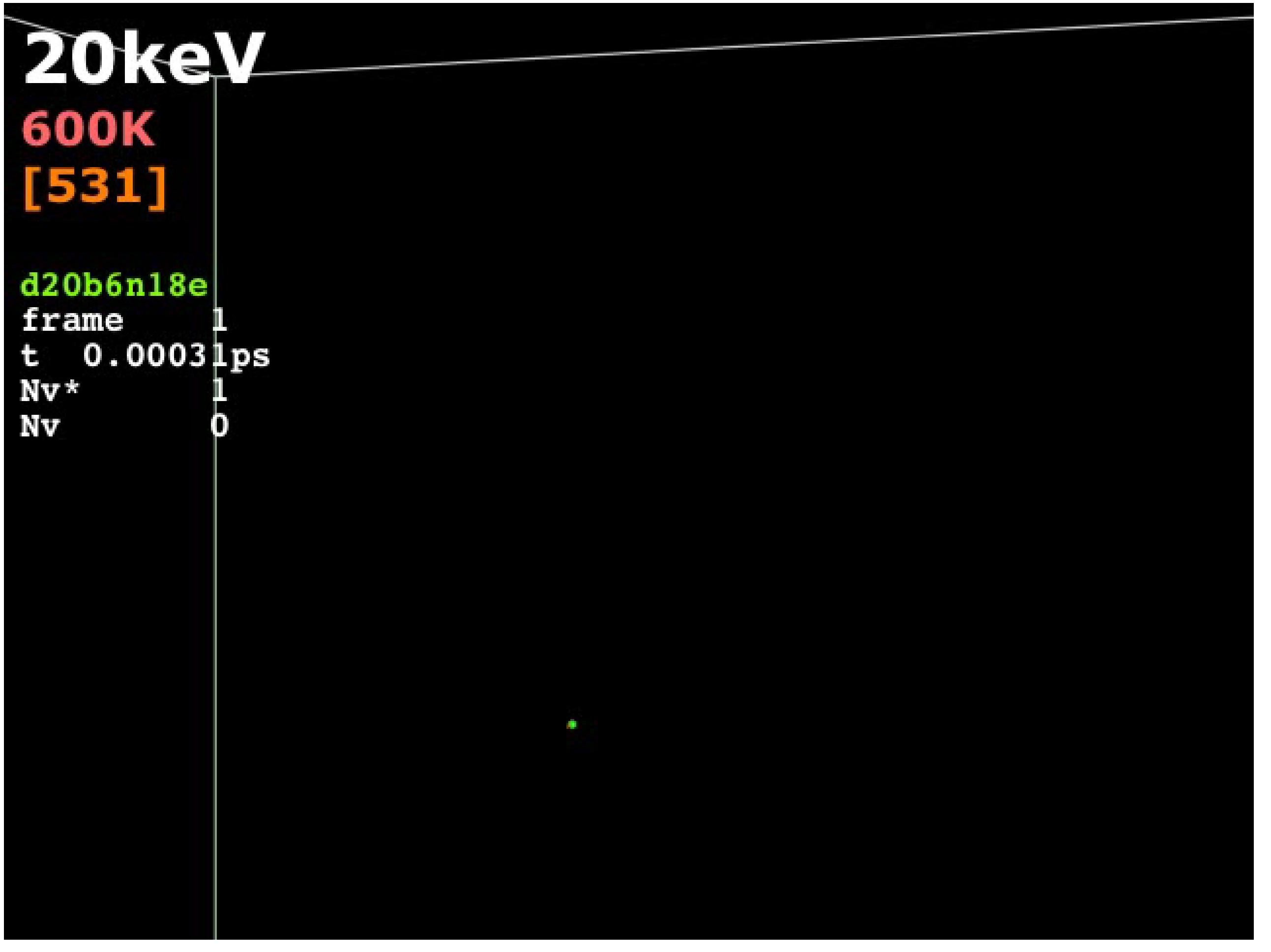
Statistical mechanics

Classical mechanics

Quantum mechanics

*http://jolisfukyu.tokai-sc.jaea.go.jp/fukyu/mirai-en/2009/5_3.html

An example) Displacement of atoms induced by irradiation



*http://www.youtube.com/watch?v=0btHd_8JFV4

These topics are covered in other courses, such as "Introduction to nuclear materials" and some graduate course.

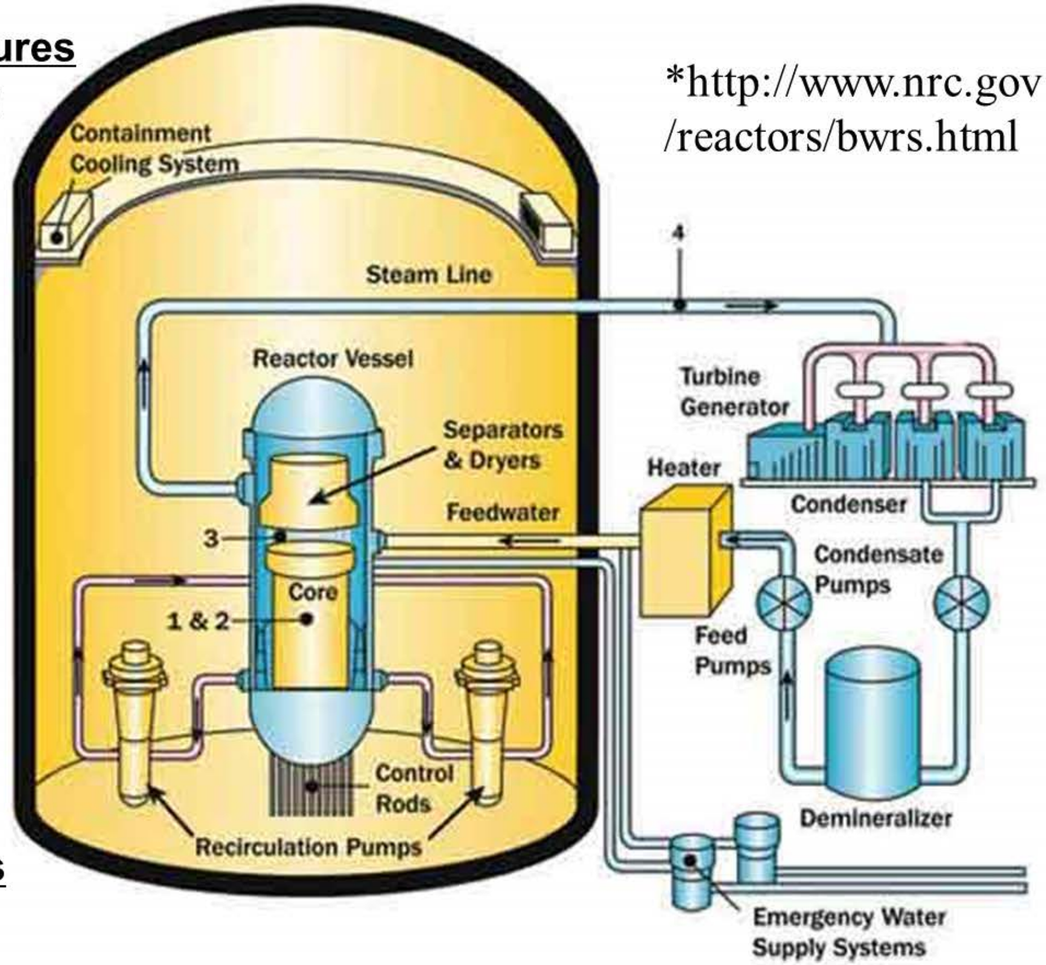
Other related topics for nuclear reactors

(1) Reactor internal structures
- ✓ Stress corrosion cracking (SCC)
- ✓ Irradiation-assisted SCC (IASCC)
- ✓ Irradiation embrittlement

(2) Fuel cladding
- ✓ Corrosion
- ✓ Hydrogen embrittlement

(3) Reactor vessel
- ✓ Irradiation embrittlement
- ✓ SCC
- ✓ Fatigue

(4) (Primary) coolant pipes
- ✓ Corrosion
- ✓ SCC
- ✓ Fatigue



(*) Cables
- ✓ Degradation in insulation

These topics are covered in some graduate course.

Contents of today

1. What is Physical Chemistry?
2. Physical Chemistry in Nuclear Engineering
3. Outline of this course
4. Short introduction of topics

Goals of today's lecture

- ✓ Understand what is Physical Chemistry.
- ✓ Understand what we are going to learn in this course.

Outline of this course (1/3)

Physical chemistry is one of important scientific disciplines in nuclear engineering. It gives systematic understanding on phenomena/processes seen in nuclear power plants and related facilities, such as degradation of nuclear materials, fuel processing and reprocessing, etc.

As reflected in the name, Physical Chemistry deals with chemical systems based on concepts and laws of physics, such as classical mechanics, thermodynamics, statistical thermodynamics, and so on.

In this course, fundamental concepts and theories in Physical Chemistry are introduced. We focus on three topics:

(1) thermodynamics,
(2) equilibrium theory, and
(3) chemical equilibrium and kinetics,

emphasizing on the connectivity among these different concepts and theories. Each topic is taught over around 4 weeks, including homework and exam.

Outline of this course (1/3)

By completing this course, we expect that participants will

(i) learn key concepts and theories in Physical Chemistry,

(ii) acquire skills to utilize laws and principles in Physical Chemistry,

(iii) understand the connectivity of multiple concepts and theories, and

(iv) get some sense on how to use these concepts and theories to interpret phenomena observed in nuclear power plants and related facilities.

Outline of this course (1/3)

Pre-requirement: none.
Textbooks/References: Donald A. McQuarrie and John D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Classroom: 33-230
Time: 11:00-12:15 on Monday and Wednesday
Instructor: Assoc. Prof. Takuji Oda (32-218, oda@snu.ac.kr)
TA: Mr. 이현석 (falconv@snu.ac.kr)

Evaluation elements: 20% for participation, 25% for homework, 55% for exams. Details will be explained in the first class.

*Although the evaluation elements of participation is around 20%, students will get F if being absent more than 1/3 of classes, according to the university regulation.

매 학기 수업일수의 3분의 2 이상을 출석하지 아니한 교과목의 성적은 “F” 또는 “U”가 된다. 다만, 불가피한 사유로 출석하지 못한 경우는 예외로 한다.(2018. 9. 1.자 시행)

Textbook contents (1/2)

-"Physical Chemistry: A Molecular Approach", McQuarrie & Simon-

Quantum physics/chemistry

1. The Dawn of the Quantum Theory
2. The Classical Wave Equation
3. The Schrodinger Equation and a Particle In a Box
4. Some Postulates and General Principles of Quantum Mechanics
5. The Harmonic Oscillator and the Rigid Rotator : Two Spectroscopic Models
6. The Hydrogen Atom
7. Approximation Methods
8. Multi-electron Atoms
9. The Chemical Bond : Diatomic Molecules
10. Bonding in Polyatomic Molecules
11. Computational Quantum Chemistry
12. Group Theory : The Exploitation of Symmetry

Application of Quantum physics/chemistry

13. Molecular Spectroscopy
14. Nuclear Magnetic Resonance Spectroscopy
15. Lasers, Laser Spectroscopy, and Photochemistry

Textbook contents (2/2)

-"Physical Chemistry: A Molecular Approach", McQuarrie & Simon-

Course schedule (revised after the class) (1/3)

Lecture #	Date	Contents
1	3-Sep	Introduction
2	5-Sep	1. Thermodynamics: Basic concepts of thermodynamics
3	10-Sep	1. Thermodynamics: The first law of thermodynamics
4	12-Sep	1. Thermodynamics: Thermodynamic process and cycle
5	17-Sep	1. Thermodynamics: The second and third laws of thermodynamics-1
6	19-Sep	1. Thermodynamics: The second and third laws of thermodynamics-2
	24-Sep	No lecture (holiday)
	26-Sep	No lecture (holiday)
7	1-Oct	1. Equation of state of gas
	3-Oct	No lecture (holiday)
8	8-Oct	Answer of homework-1
9	10-Oct	Exam-01 (2 hour)
10	15-Oct	2. Introduction to equilibrium theory
11	17-Oct	2. Free energy-1
12	22-Oct	2. Free energy-2
13	24-Oct	2. Calculation of thermodynamic quantities
	29-Oct	No lecture
	31-Oct	

Course schedule (revised after the class) (2/3)

	29-Oct	No lecture
	31-Oct	
14	5-Nov	2. Phase equilibrium-1
15	7-Nov	2. Phase equilibrium-2
16	12-Nov	2. Phase equilibrium-3
17	14-Nov	Answers of homework-2
18	19-Nov	Exam-02 (2 hour)
19	21-Nov	3. Chemical equilibrium-1
20	26-Nov	3. Chemical equilibrium-2
21	28-Nov	3. Chemical equilibrium-3
22	3-Dec	3. Chemical kinetics-1
23	5-Dec	3. Chemical kinetics-2
24	10-Dec	3. Chemical kinetics-3
25	12-Dec	Answers of homework-3
26	17-Dec	Exam-03 (2 hour)

Course schedule (tentative) (3/3)
- examination and homework -

<Examination>

#	Subject	Exam
1	Thermodynamics	10/10
2	Equilibrium theory	11/19
3	Reaction kinetics / Rate theory	12/17

<Homework>

#	Subject	Problems upload	Submission deadline	Answer check
1	Thermodynamics	9/19	10/1	10/8
2	Equilibrium theory	10/24	11/7	11/14
3	Reaction kin. / Rate theo.	11/26	12/5	12/12

*These dates may be changed !!

- ✓ I also update a lecture note 2 days before the lecture.
  - ✓ For a Monday lecture, till Saturday night.
  - ✓ For a Wednesday lecture, till Monday night.

Contents of today

1. What is Physical Chemistry?

2. Physical Chemistry in Nuclear Engineering

3. Outline of this course

4. Short introduction of topics

Goals of today's lecture

- ✓ Understand what is Physical Chemistry.
- ✓ Understand what we are going to learn in this course.

Short introduction: 1. Thermodynamics (1/4)

Thermodynamics is a branch of natural science concerned with heat and its relation to energy and work. It defines macroscopic variables (such as temperature [T], internal energy [U], entropy [S], and pressure [P]) that characterize materials and radiation, and explains how they are related and by what laws they change with time.

Thermodynamics describes the average behavior of very large numbers of microscopic constituents, and its laws can be derived from statistical mechanics.

*wikipedia

Short introduction: 1. Thermodynamics (2/4)

Thermodynamics

- ✓ treats macroscopic system (like one composed by 10^{23} atoms), not microscopic (e.g. atom, molecule, ….)
- ✓ treats macroscopic physical quantity (e.g. temperature, entropy, …), not microscopic (e.g. location of each atom).
  - ✓ can be extended to microscopic ones in statistical thermodynamics.
- ✓ treats only thermal equilibrium state, not non-equilibrium state. (may be extended though).
  - ✓ It considers a transition from one equilibrium state to another, but not non-equilibrium states usually appearing on the way. As thermodynamics cannot deal with non-equilibrium state, it cannot treat the transition of states.
- ✓ focuses on macroscopic physical quantity.
  - ✓ V: volume , P: pressure, T: temperature, E: energy, N: number of atoms
  - ✓ H: enthalpy, S: entropy, A: Helmholtz (free) energy, G: Gibbs (free) energy.

Short introduction: 1. Thermodynamics (3/4)

Thermodynamics are based on several laws, mainly on the famous "the first/second/third law of thermodynamics".

- ✓ The zeroth law
  : concept of equilibrium state, definition of temperature
- ✓ The first law (textbook $19)
  :energy conservation, equivalence of work and heat (as energy quantity)

$$dU = \delta q + \delta w, \quad \Delta U = \delta q + \delta w$$

- ✓ The second law (textbook $20)
  :introduction of entropy, direction toward an equilibrium state, quality of energy

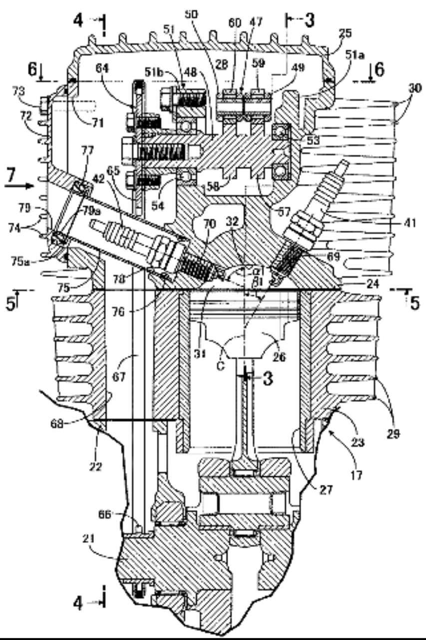
$$dS \geq \frac{\delta q}{T}$$

- ✓ The third law (textbook $21)
  :definition of the absolute value (standard value) of entropy (the entropy of a perfect crystal at absolute zero (K) is zero.)

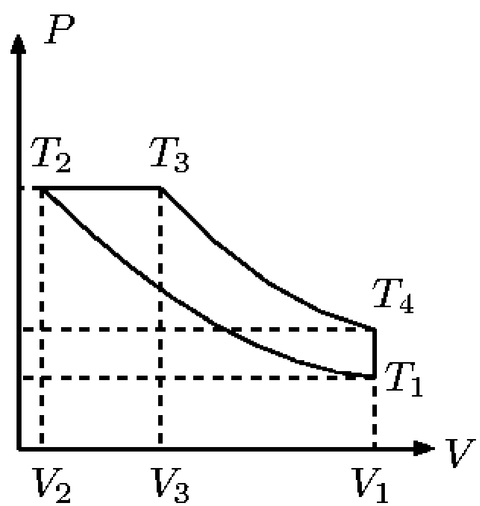
Short introduction: 1. Thermodynamics (4/4)

- ✓ The principles to learn in this thermodynamics topic constructs bases of more applied concepts (equilibrium, kinetics / rate theory).
- ✓ But it can be also directly utilized to evaluate the efficiency of a power cycle for automobiles, power plants, etc.

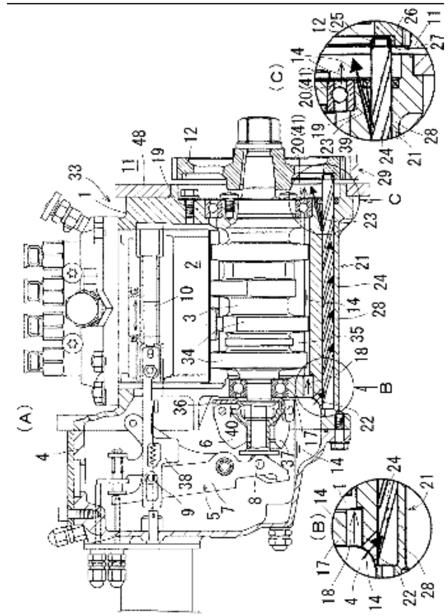
Spark-ignition engine
for Otto cycle



Which is better?
(theoretically)



Diesel engine
for Diesel cycle



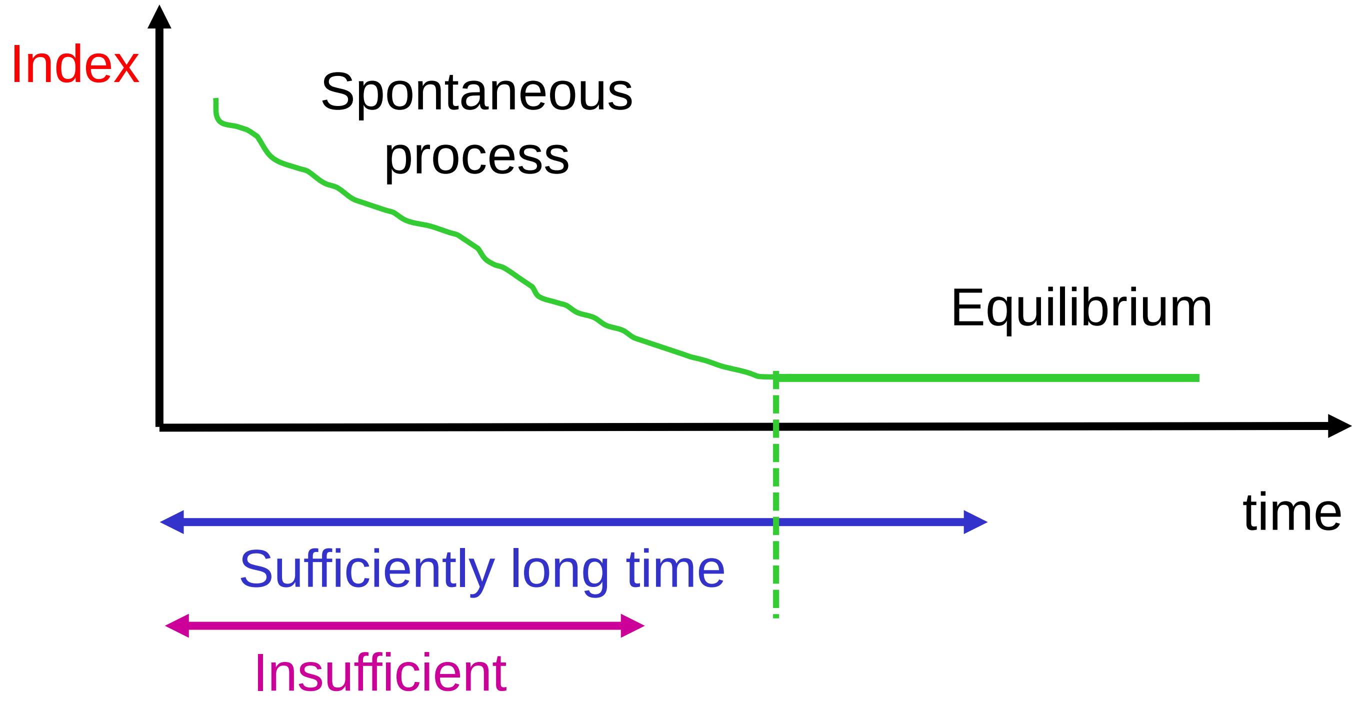
http://astamuse.com/ja/published/JP/

Short introduction: 2. Equilibrium theory (1/3)

In practical situation, we often want to know

"what products (matters) we can obtain after mixing multiple raw materials and then waiting for a sufficiently long time".

Here, "a sufficient long time" means that the time is long enough to achieve equilibrium state.



Short introduction: 2. Equilibrium theory (2/3)

Free energy (as well as entropy) is a good index to predict the equilibrium state and the direction of reaction.

We have two important free energies:

- ✓ Helmholtz energy (A)

  : for a system of constant T, constant V

$$A = U - TS$$

- ✓ Gibbs energy (G)

  : for a system of constant T, constant P

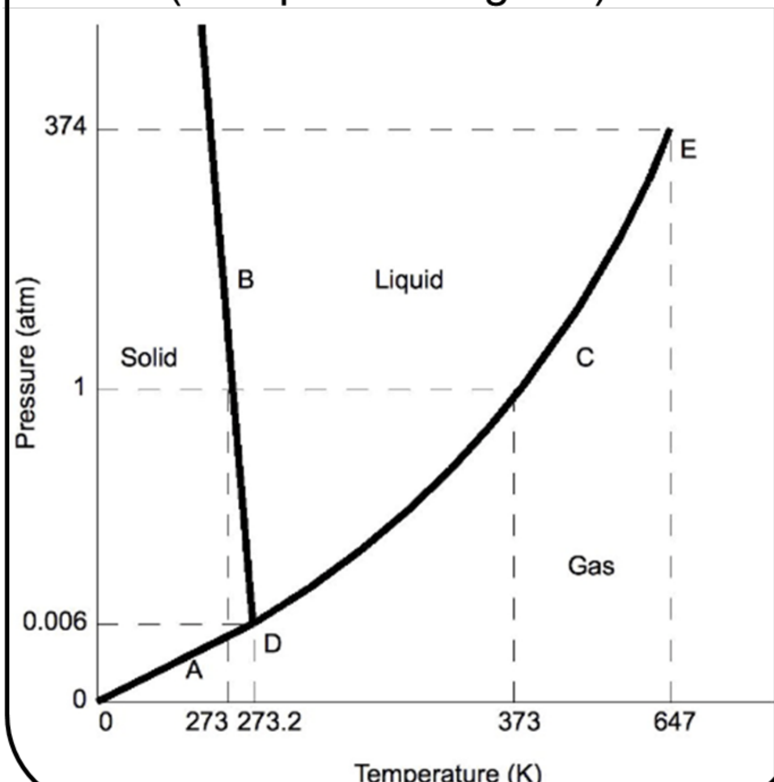
$$G = H - TS = A + PV$$

Short introduction: 2. Equilibrium theory (3/3)

We are going to see applications of what we studied in Section 1 and then learn two examples for equilibrium.

1. Phase equilibrium

(with phase diagram)



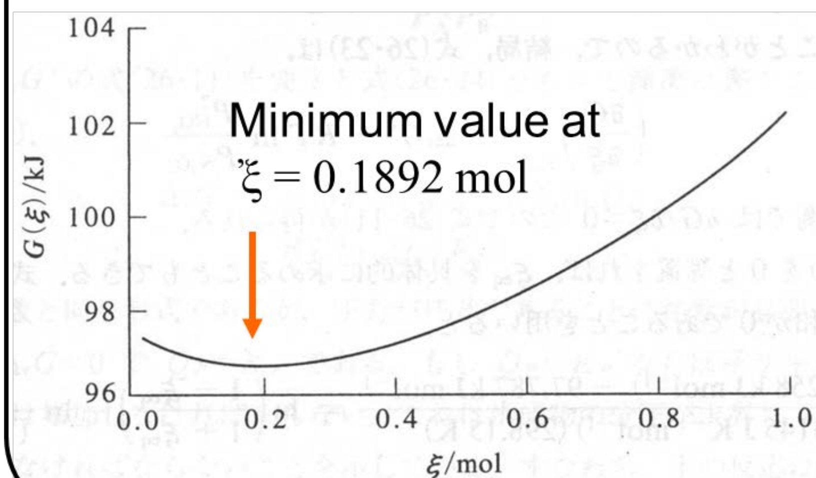
2. Chemical equilibrium

$N_2O_4(g) \rightleftarrows 2NO_2(g)$

*at $26.4

$N_2O_4(g)$: $1-\xi$ mol

$NO_2(g)$: 2ξ mol



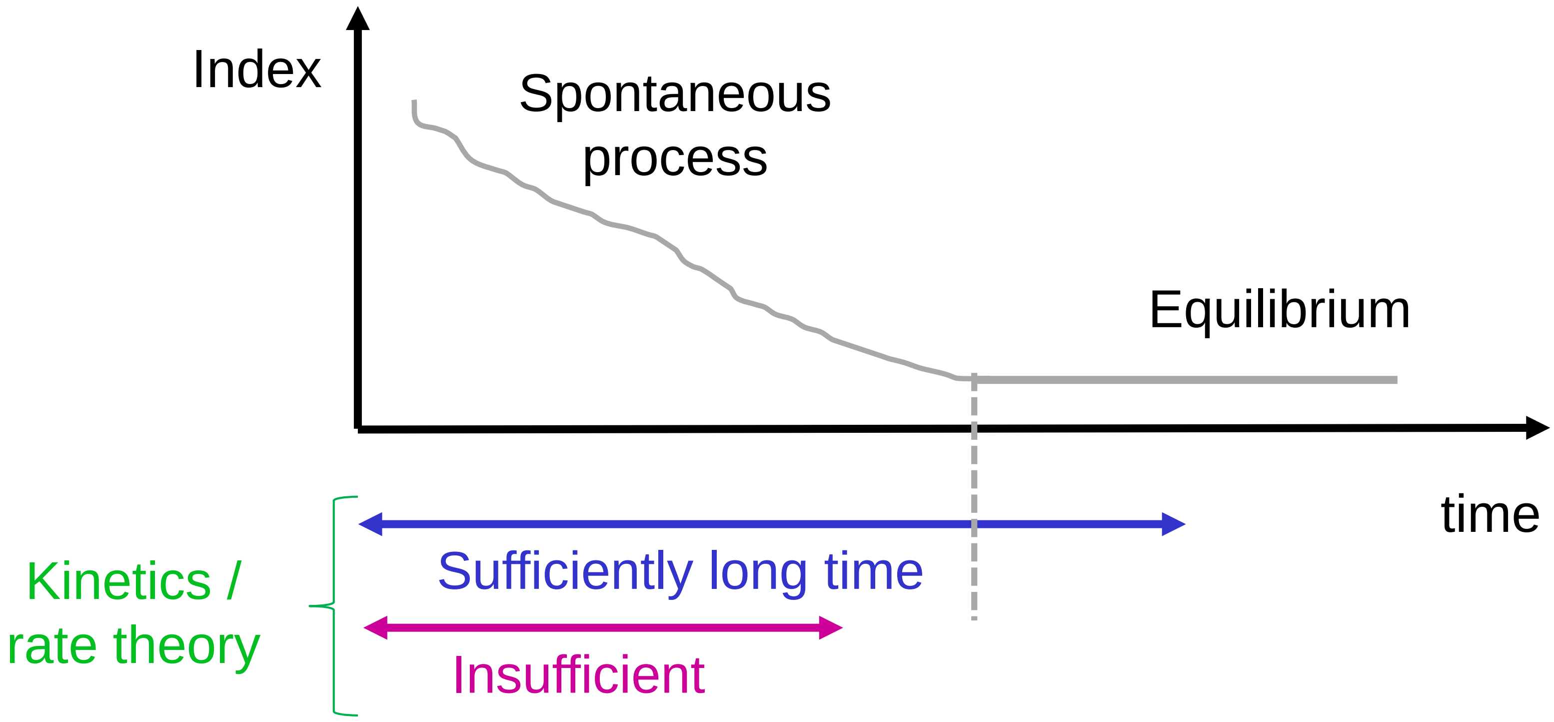
http://chemwiki.ucdavis.edu/Physical_Chemistry

D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

Short introduction: 3. Kinetics / Rate theory (1/3)

Equilibrium theory is powerful, but it cannot indicate how long it take to reach the equilibrium state.

Kinetics and rate theory can analyze and give information on the speed (=rate) of a reaction.



Kinetics and rate theory are mostly based on thermodynamics, but can be extended to microscopic systems (via statistics mechanics/thermodynamics).

Short introduction: 3. Kinetics / Rate theory (2/3)

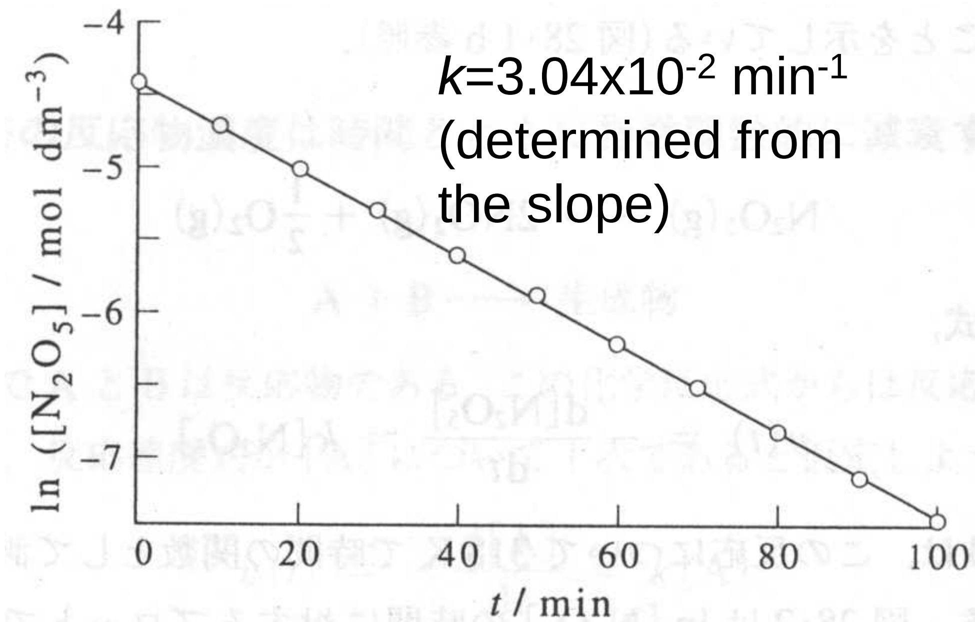
- ✓ Kinetics and rate theory are mostly based on thermodynamics, but they are often applied to microscopic systems through statistics mechanics/thermodynamics, etc.

$N_2O_5(g) \rightleftarrows 2NO_2(g) + ½\ O_2\ (g)$

*at $28.3

$$v(t) = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

v(t): rate of reaction
k: rate constant



D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Short introduction: 3. Kinetics / Rate theory (3/3)

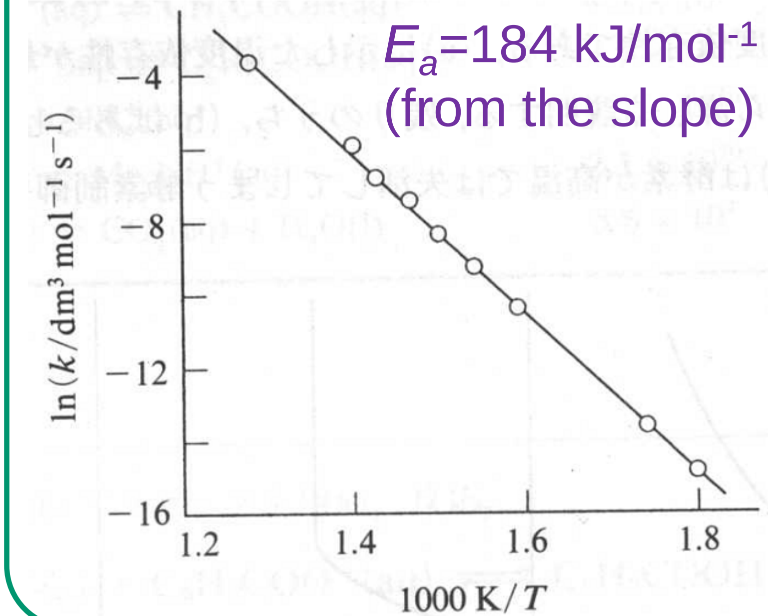
$2HI(g) \rightleftarrows H_2(g) + I_2(g)$

*at $28.7

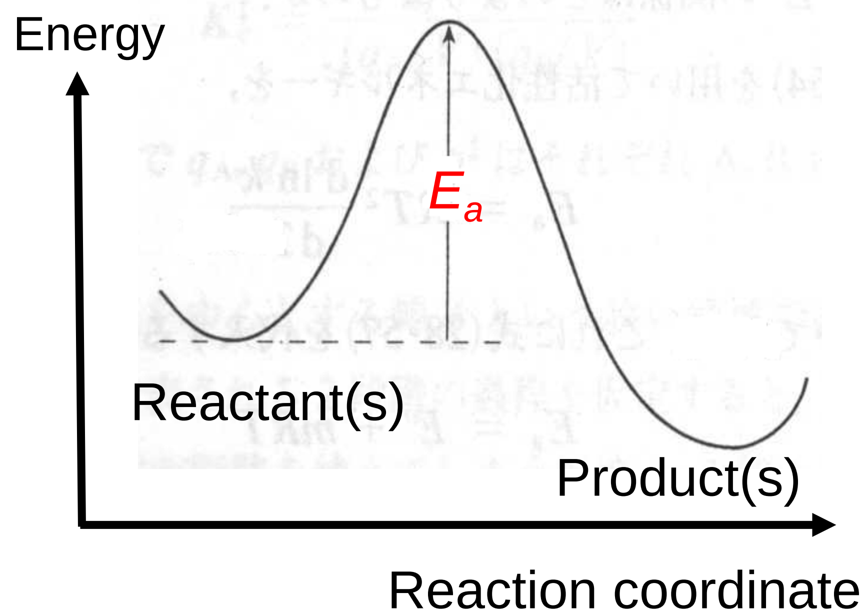
Temperature dependence of rate constant gives activation energy (E_a).

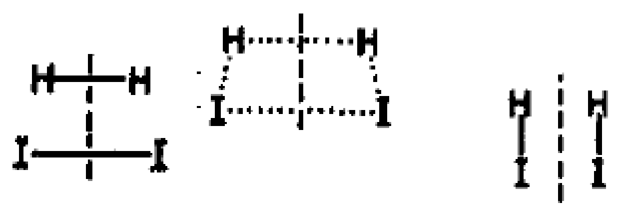
$$k = A \times exp(-E_a/RT)$$

E_a=184 kJ/mol^{-1}
(from the slope)



Connection with quantum chemistry and transition theory





*R. Hoffmann, J. Chem. Phys. 49, 3739 (1968).

D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

What we do not study although they are important

<Quantum Mechanics>

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

$$\hat{\mathcal{H}}\psi = E\psi$$

Using Schrodinger equation, we can determine the energy of a system and then the motion of atoms!

<Statistical mechanics/thermodynamics>

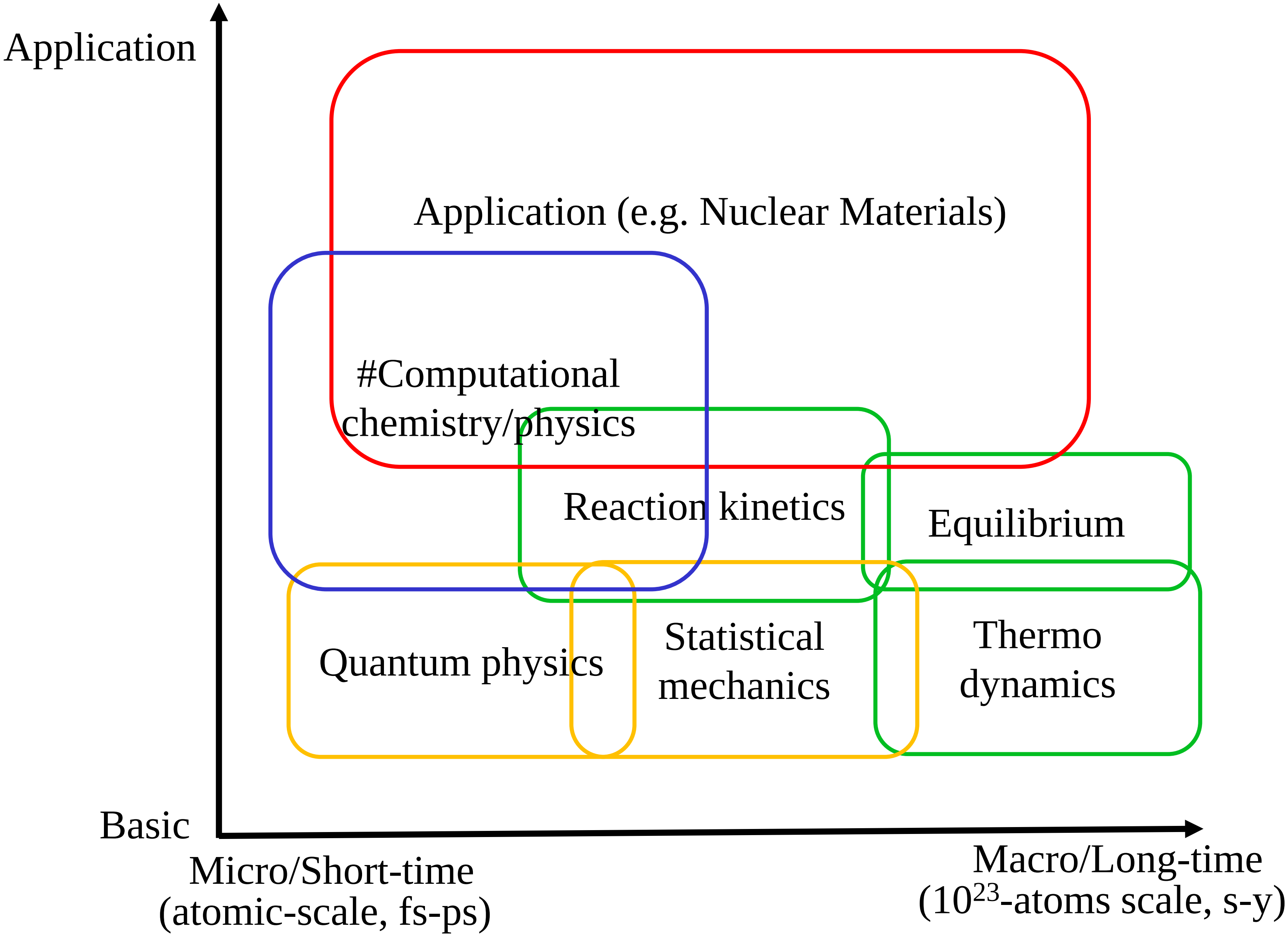
$$Z = \sum_j \exp\{-\varepsilon_j/(k_B T)\}$$

$$F = U - TS = -k_B T \ln Z$$

$$S = k_B T\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N} + k_B \ln Z$$

Using a partition function, we can determine thermodynamic quantities, such as free energy, entropy etc.
We can connect micro and macro!

Summary of “what we are going to learn”



Summary of "what we are going to learn"