


Study Guide Thermodynamics (Physical Chemistry 1) (MOL135) 2021/2022

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Literature

- Book: Physical Chemistry; P.W. Atkins; edition 11, 10, 9 or 8, Oxford University Press
- Study guide: will be made available online during the course
- All information will be available via the link in Brightspace or directly at <http://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html>



Aim

- Primary: Insight and skills
- Secondary: Knowledge




Organisation

- **Lectures.** During the lectures particularly the more difficult parts of the book will be emphasized. Furthermore, extra subjects that are not dealt with in the book will be treated. If necessary, these subjects will be incorporated in the study guide.
NB., thus the study guide is NOT a summary of ALL subjects.


- **Tutorial Classes.** Every week there will be one-hour Tutorial Classes (Q&A in the schedule) directly after the lunch break. The MS-tutors will then be present to answer questions and to help in solving exercises. This will involve extra exercises rather than exercises from the Exercise Classes (see next item).


The division into Tutorial Classes will be the same as in previous quarters; others are free to join.

Tutor	Els Heijmen	Martin Waals	Ade Hoekstra	Yvette van Rijckevorsel	André Steenberg
Location	HG00.622	HG00.308	HG00.062	HG00.616	HG00.071
Capacity	50	28	63	50	63
Language	Dutch	Dutch	English	English	English

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- **Exercise Classes.** The exercises for both the Tutorial Classes and the Exercise Classes will be distributed in the lectures; answers will be available online after the Exercise Classes. The answers to the exercises do not have to be handed in. The level of the most difficult exercises is comparable to the most difficult exercises in the book and reflects the level of the problems in the exam. The five groups are the same as for the tutorials; others are free to join.

Location	HG00.622	HG00.308/310	HG00.062	HG00.616	HG00.071
Stud.Ass.	Niek Aarts	Shen van Hassel	Xiamei Klančnik	Sanne Kusters	Cas de Leeuw
Tutor	Els Heijmen	Martin Waals	Ade Hoekstra	Yvette van Rijckevorsel	André Steenberg

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- **Evaluation.** The final evaluation will solely be determined by the exam, which consists of 4 exercises with 4 questions each. All 16 parts have equal weight for the final mark. An example exam (without answers) will appear online at the end of the lectures series. A list of formulae (Appendix C), without further comments will be provided at the exam. Graphical calculators are NOT allowed during the exam (regular ones are).

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- **Video recordings.** There will be no video recordings of the lectures (recordings of 2020/2021 will be put on Brightspace), primarily to promote the study efficiency and especially to promote studying of the book. During the course only subjects will be dealt with that are either in the book or in the study guide (see Table 1, 2 or 3).

Formulae

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\Delta U = W + Q$$

$$dW = -P_{ext}.dV + dW' \quad \text{and} \quad dW'_{max} = (dG)_{P,T}$$

$$dQ|_P = C_P dT \quad \text{and} \quad dQ|_V = C_V dT$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$dS = \frac{dQ^{rev}}{T} \geq \frac{dQ}{T}$$

$$dS_{tot} = dS + dS_{env} \geq 0$$

$$dU = -PdV + TdS + \sum_i \mu_i dn_i$$

$$H = U + PV$$

$$dH = VdP + TdS + \sum_i \mu_i dn_i$$

$$A = U - TS$$

$$dA = -PdV - SdT + \sum_i \mu_i dn_i$$

$$G = H - TS$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \Delta_r G^\ominus + RT \ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT \ln K = -\Delta_r G^\ominus$$

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad dW' = Edq \quad \text{furthermore} \quad E = IR \quad \text{and} \quad P = EI$$

$$\mu_i = \mu_i^\ominus + RT \ln a_i = \mu_i^\ominus + RT \ln \frac{P_i}{P^\ominus}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j d\mu_j = 0$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{trs} H} \right) x_B$$

$$\Delta S = -nR (x_A \ln x_A + x_B \ln x_B)$$

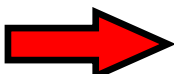
$$\Pi = [B]RT = \frac{n_B}{V} RT$$

$$S = k \ln W$$

$$\frac{n_i}{N} = \frac{\exp \frac{-\epsilon_i}{kT}}{q} \quad \text{with} \quad q = \sum_i \exp \frac{-\epsilon_i}{kT} \quad \text{and} \quad \langle X \rangle = N \langle x \rangle = N \sum_i x_i \frac{n_i}{N}$$

Subjects that will be treated

The time schedule for the various topics of Thermodynamics will become clear from the tables below for the different editions of Atkins.



Day	Sections (edition 11 Atkins)	Subject
11/11	1A + 1C + 2A + 2B (+ 2E) + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
18/11	3A + 3B + 3D1 + 3E2a-c + SG9-13	Entropy, Second Law of Thermodynamics Free energy, Irreversible processes
25/11	5A1b-c + SG14-16 2C + 3D2a + 6A	Chemical Potential, Activity Thermochemistry, Chemical Equilibria
02/12	6B 6C1-3 + 6D(p.224)	<i>T, P</i> -dependence equilibria Electrochemistry, Standard Potential, Nernst-equation
09/12	5B + 5F1-2 + SG17-18	Mixtures, Colligative properties
16/12	3A3 + SG19-22	Second Law of Thermodynamics, Efficiency
23/12	3B + 3C + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

Table 1: Overview of the topics treated from edition 11 of Atkins; SG*i*: page *i* of the study guide

Day	Sections (edition 10 Atkins)	Subject
11/11	1A + 1C + 2A + 2B (+ 2E) + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
18/11	3A + 3C1 + 3D2a-c + SG9-13	Entropy, Second Law of Thermodynamics Free energy, Irreversible processes
25/11	5A1b-c + SG14-16 2C + 3C2a + 6A	Chemical Potential, Activity Thermochemistry, Chemical Equilibria
02/12	6B 6C1-3 + 6D(p.267)	<i>T, P</i> -dependence equilibria Electrochemistry, Standard Potential, Nernst-equation
09/12	5B + 5E1-2 + SG17-18	Mixtures, Colligative properties
16/12	3A3 + SG19-22	Second Law of Thermodynamics, Efficiency
23/12	3B + 3C + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

Table 2: Overview of the topics treated from edition 10 of Atkins; SG*i*: page *i* of the study guide

Day	Sections (edition 9 Atkins)	Subject
11/11	1.1 - 1.4 + 2.1 - 2.6 + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
18/11	3.1 - 3.3a + 3.5 + 3.9 + SG9-13	Entropy, Second Law of Thermodynamics Free energy, Irreversible processes
25/11	5.1b-c + SG14-16 2.7 - 2.9 + 3.6 + 6.1-6.2	Chemical Potential, Activity Thermochemistry, Chemical Equilibria
02/12	6.3 - 6.4 6.5 - 6.8	<i>T, P</i> -dependence equilibria Electrochemistry, Standard Potential, Nernst-equation
09/12	5.4-5.5 + 5.10-5.11 + SG17-18	Mixtures, Colligative properties
16/12	3.2 + SG19-22	Second Law of Thermodynamics, Efficiency
23/12	3.3 - 3.4 + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

Table 3: Overview of the topics treated from edition 9 of Atkins; SG*i*: page *i* of study guide

Recommendations regarding study attitude

The aim of the course has already been summarized on page 1 of the study guide :

Primary: insight and skills and secondary: knowledge

This means (some definitions will not be familiar yet):

- Insight is obtained by studying the material but particularly also by actively solving the problems in the tutorials.
Insight into the backgrounds of the laws of Thermodynamics as well as the concepts that result from these laws is necessary.
What do the symbols in a formula stand for?
Under what circumstances can I apply a certain formula?
How can I exploit a state function; is the process irreversible or reversible?
When can I choose an alternative path for a certain process?
- Skills are obtained by actively solving exercises and problems and reflecting back on the insights gained:
How do I solve a problem?
Which paths are most suitable in a certain process?
How do I compose a total differential?
Can or should I calculate in moles?
Can I replace an irreversible process by a reversible process?
- Knowledge is less important.
The list of definitions from the beginning of the course containing concepts as system, bath, closed system, etc. are part of prepared knowledge, but also things like 'the work done *on* the system is positive' or 'adiabatic means $dQ = 0$ ', or ' S is a state function'.
Formulae are *not* part of prepared knowledge; do not spend any unnecessary energy in learning formulae by heart, you will have all relevant formulas available during the exam!

At the exam a list of formulae (Appendix C) without further comments will be provided. In principle this list will contain all relevant formulae necessary to complete the exercises. However, the list will also contain formulae that are not necessary. Insight and skills will allow you to choose and apply the right formulae.

Glossary

Microscopic On an atomic or molecular scale.

Macroscopic Seen from an helicopter view, in such a way that we can forget about microscopic processes (averaging).

System That part of the universe in which we are interested; we only consider macroscopic systems with many particles in thermodynamics.

Surroundings The rest of the universe we need to allow exchange of matter or energy with the system; is also a system, but not *the* system.

Thermal bath A heat reservoir (usually as surroundings), from which you can extract heat or to which you can deliver heat, without changing the temperature of the reservoir.

State variables Macroscopic quantities (P, V, T, n, \dots) that describe the thermodynamic state of a system. For a complete description a minimal amount of (independent) state variables is required.

Equation of state Relation between state variables that determines the possible states of the system in thermodynamic equilibrium.

Thermodynamic equilibrium A system is in thermodynamic equilibrium if the state variables of the system do not change spontaneously.

State function A (thermodynamic) single valued function of the (independent) state variables; The value of a state function is independent of the way the system has reached a certain state.

Reversible process A process during which the system is in thermodynamic equilibrium at every moment; with that a reversible process is also reversible.

Irreversible process A process that is not necessarily reversible.

Isothermal process A process that proceeds at constant temperature ($dT = 0$ for the system).

Isobaric process A process that proceeds at constant pressure ($dP = 0$ for the system).

Isochoric process A process that proceeds at constant volume ($dV = 0$ for the system).

Adiabatic process A process that proceeds without heat exchange with the environment ($dQ = 0$).

Isolated system No exchange between system and surroundings ($dW = dQ = dn = 0$).

Closed system No exchange of matter between system and surroundings ($dn = 0$); there can be exchange of work ($dW \neq 0$) or heat ($dQ \neq 0$).

Open system A non-closed system ($dn \neq 0$).

Homogeneous system A system in which every (macroscopic) subsystem has the same properties.

Isotropic system A system that has the same properties in all directions, such as an homogeneous fluid. A crystal is not isotropic.

Intensive quantity Does not change if we enlarge the system; e.g. T and P .

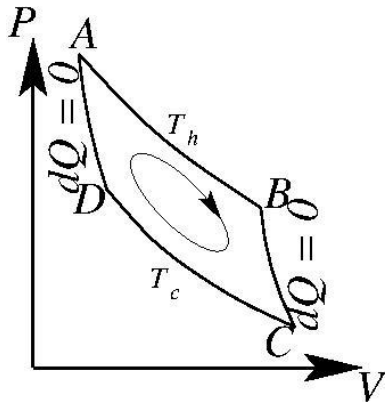
Extensive quantity Doubles if we make the system twice as large; e.g. V and n .

Statistical thermodynamics Relates microscopic processes and (macroscopic) thermodynamics.

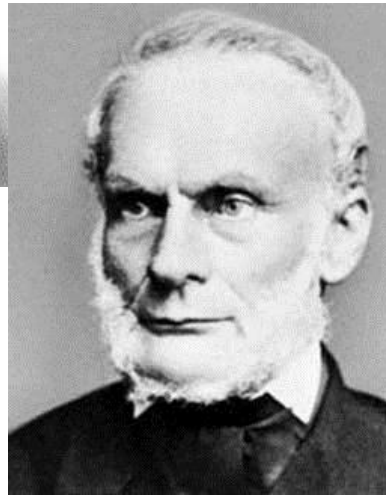
Thermodynamics governs all processes



Carnot 1824



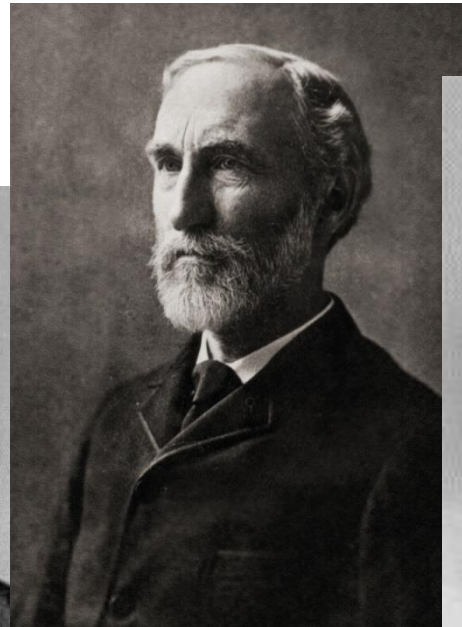
efficiency



Clausius 1856

$$dS = \frac{dQ^{\text{rev}}}{T}$$

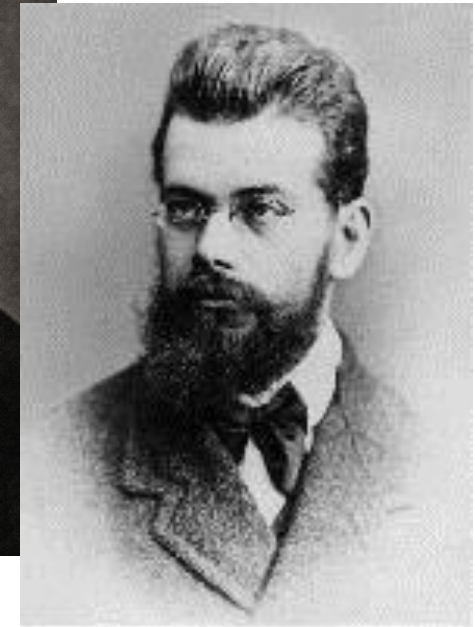
entropy



Gibbs 1870

$$G = H - TS$$

free energy



Boltzmann 1896

$$S = k \ln W$$

statistical

thermodynamics

Thermodynamics deals with large numbers



$$N_A = 6.02214 \dots \cdot 10^{23} \text{ mol}^{-1}$$

Amadeo Avogadro di Quaregna e Cerreto
(1776-1856)

Thermodynamics deals with large numbers



$$N_A = 6.02214 \dots \cdot 10^{23} \text{ mol}^{-1}$$

$$R = N_A k$$

$$k = 1.38065 \dots \cdot 10^{-23} \text{ J / K}$$

$$R = 8.31446 \dots \text{ J / mol K}$$

$$nR = Nk$$

$$N_A = \frac{R}{k} \quad (n = 1)$$

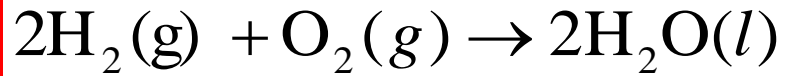
Ludwig Boltzmann (1844-1906)

Thermodynamics

Tells us whether a process will run or not
Tells us in which direction it will run

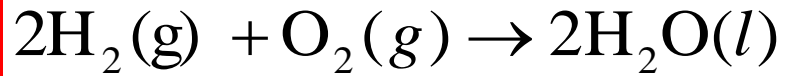
Thermodynamics

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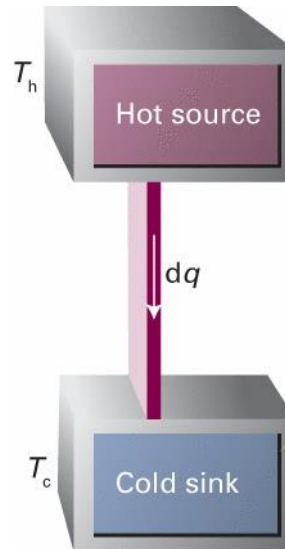
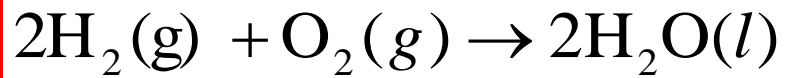
Thermodynamics

Tells us whether a process will run or not
Tells us in which direction it will run



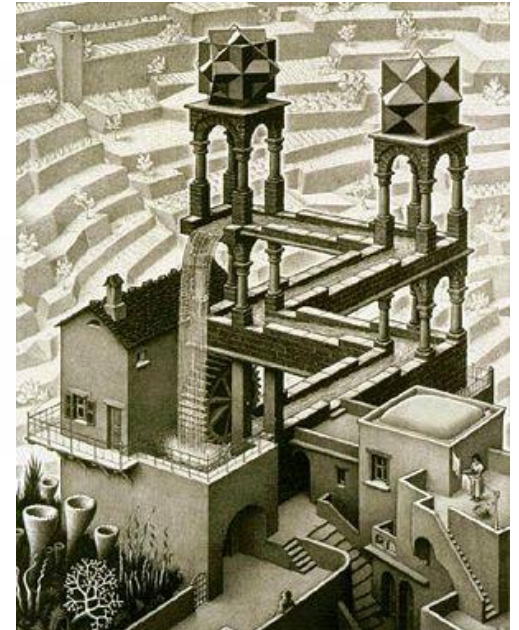
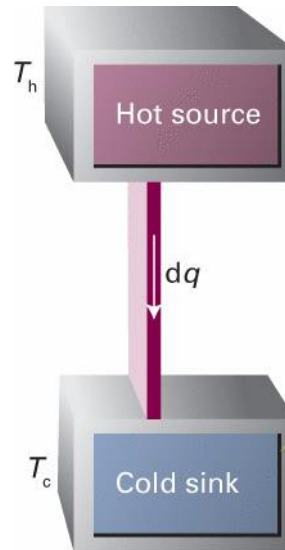
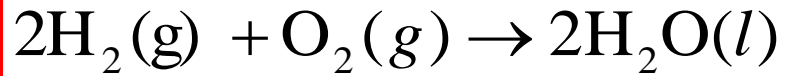
Thermodynamics

Tells us whether a process will run or not
Tells us in which direction it will run



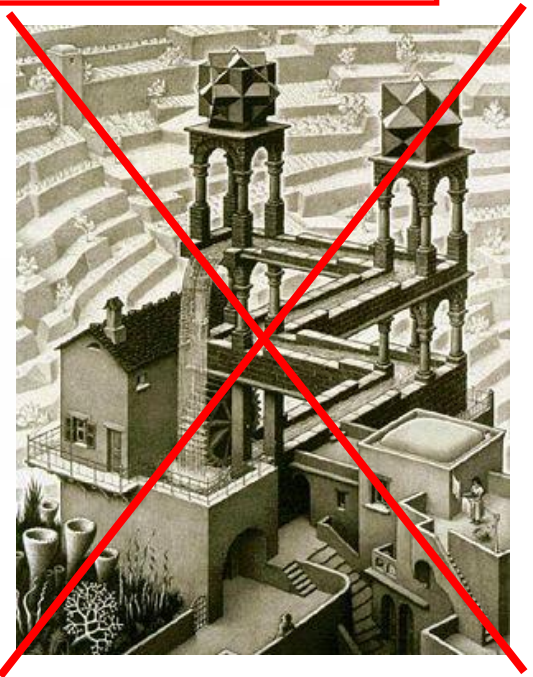
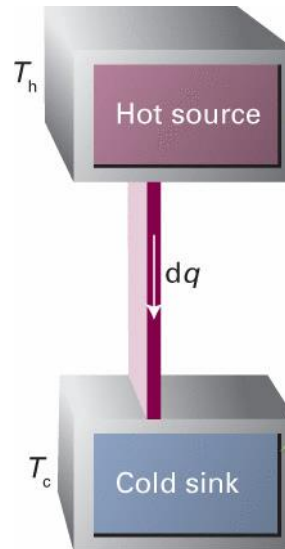
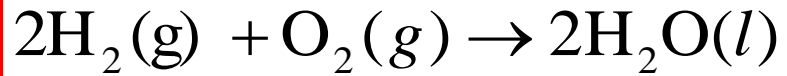
Thermodynamics

Tells us whether a process will run or not
Tells us in which direction it will run

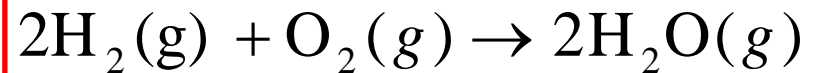


Thermodynamics

Tells us whether a process will run or not
Tells us in which direction it will run

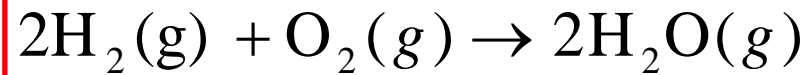


Thermodynamics is about processes

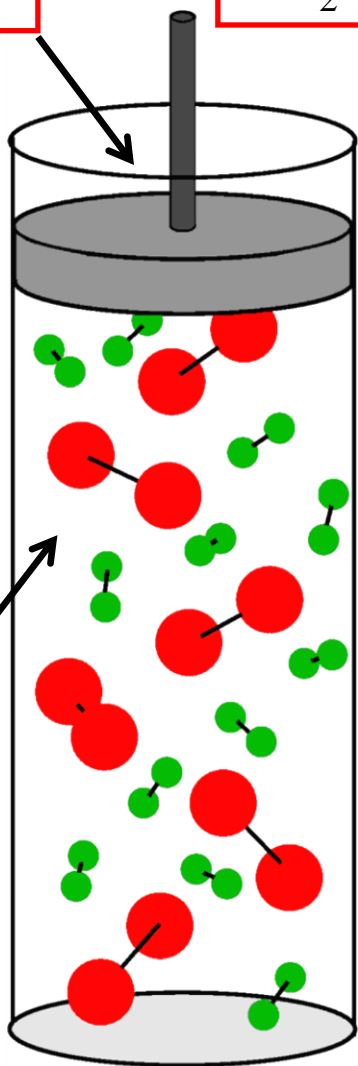


Thermodynamics is about processes

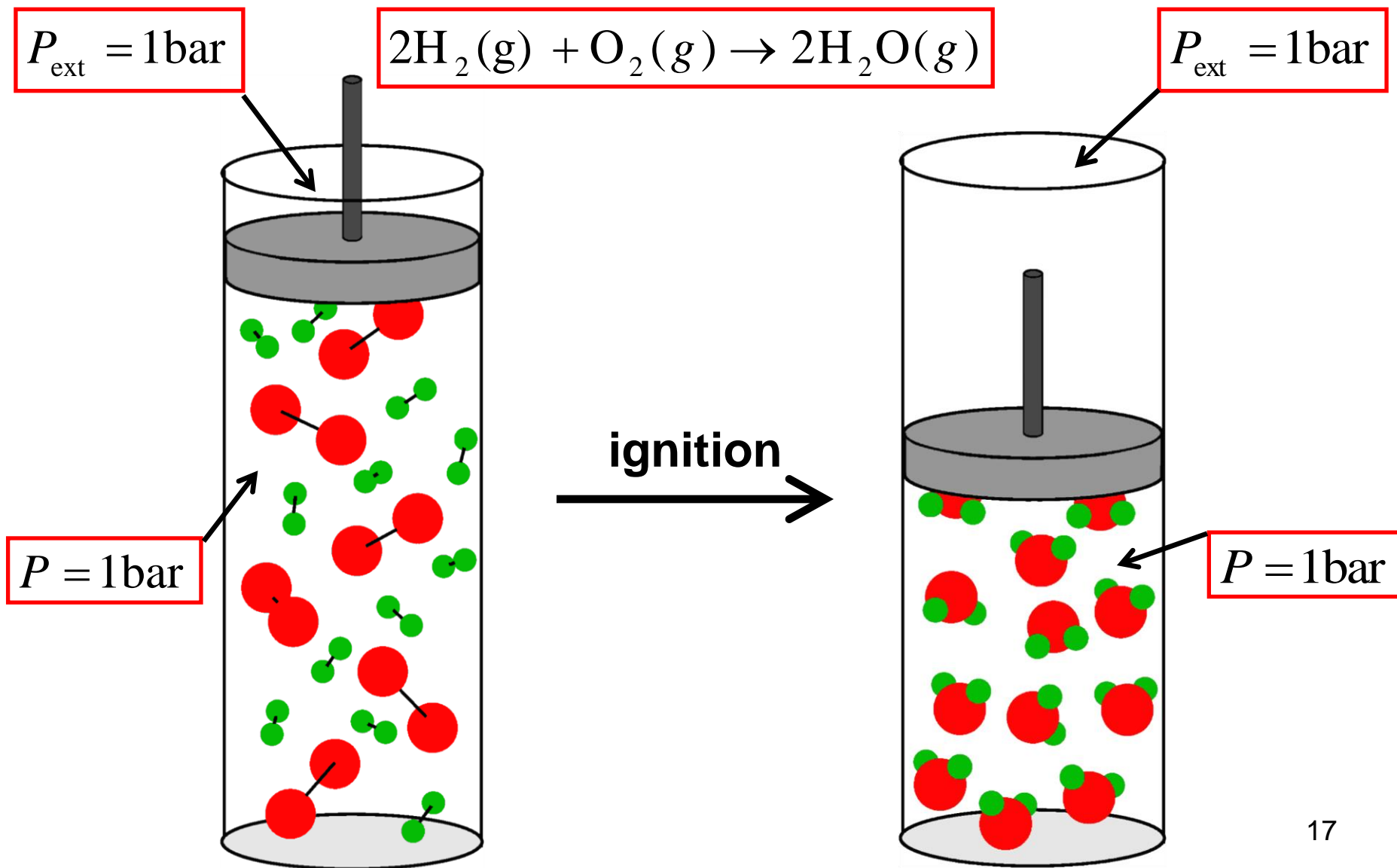
$$P_{\text{ext}} = 1\text{bar}$$



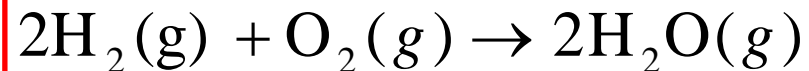
$$P = 1\text{bar}$$



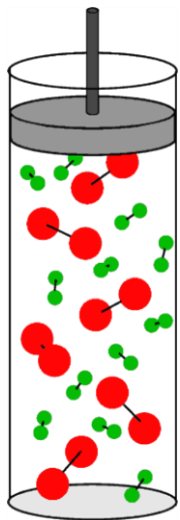
Thermodynamics is about processes



Thermodynamics is about processes



We have made a few assumptions:



Initial state

- Final state is an **equilibrium** state



$$P_{\text{final}} = P_{\text{ext}}$$

- Initial state is **quasi equilibrium** state



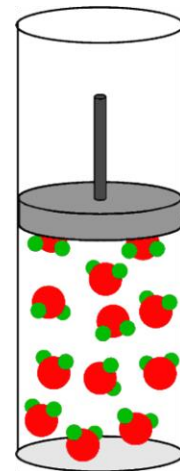
$$P_{\text{initial}} = P_{\text{ext}}$$

- The gases are **perfect gases**



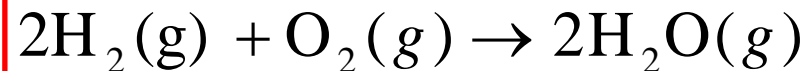
$$PV = nRT$$

- The temperature T was constant



Final state

Thermodynamics is about processes



We have made a few assumptions:

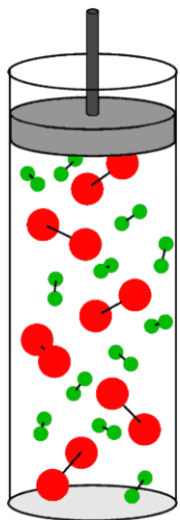
- The gases are **perfect gases**

Assume
 T is constant

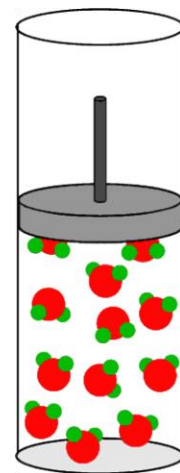


$$PV_{\text{I}} = n_{\text{I}}RT$$

$$PV_{\text{F}} = n_{\text{F}}RT$$

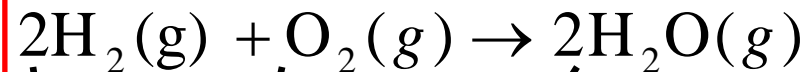


Initial state



Final state

Thermodynamics is about processes



We have made a few assumptions:

- The gases are **perfect gases**

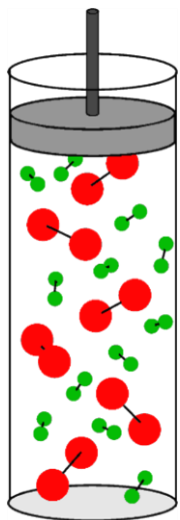
Assume
 T is constant

$$PV_{\text{I}} = n_{\text{I}}RT$$

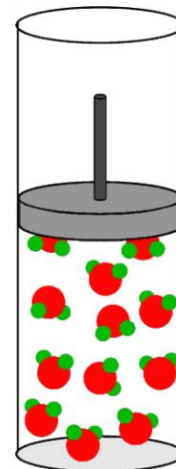
$$PV_{\text{F}} = n_{\text{F}}RT$$

$$n_{\text{F}} = \frac{2}{3} n_{\text{I}}$$

$$V_{\text{F}} = \frac{2}{3} V_{\text{I}}$$



Initial state



Final state

Perfect gases

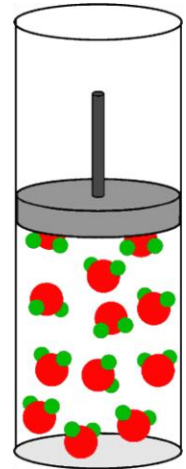
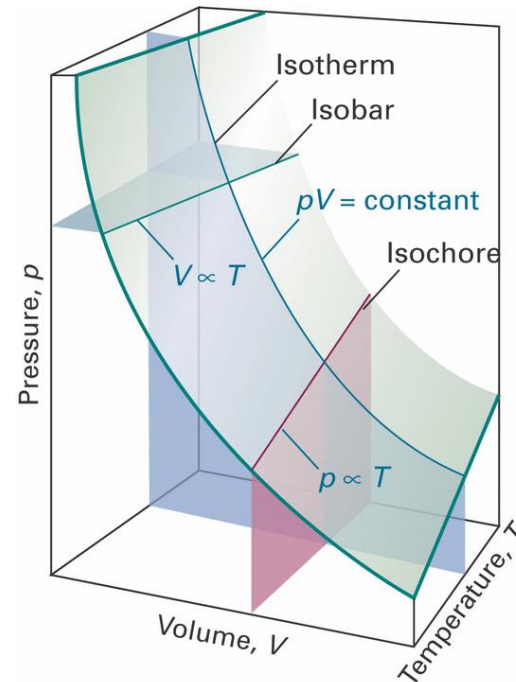
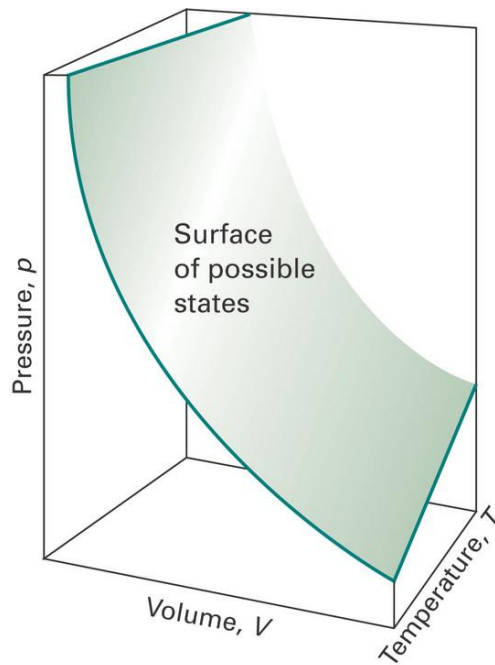
Equation of state

$$PV = nRT = NkT$$

(only valid in thermodynamic equilibrium)

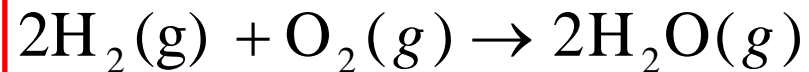
State variables

$$P, V, T, n$$



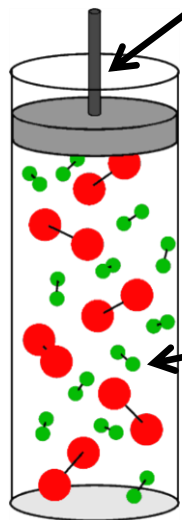
Closed system: n constant ($dn = 0$)

Thermodynamics is about processes

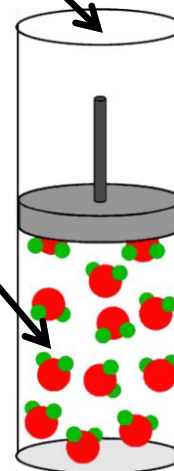


Some new definitions:

- Surroundings are external to the system:

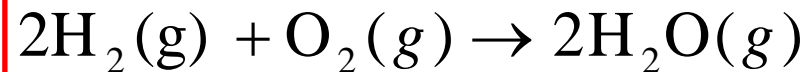


Initial state



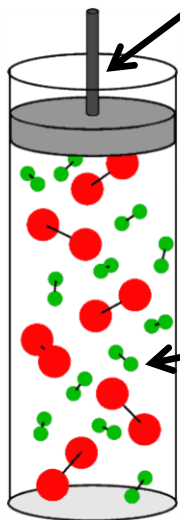
Final state

Thermodynamics is about processes

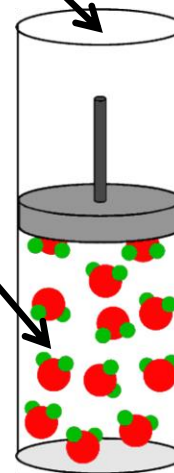


Some new definitions:

- Surroundings are external to the system:



Initial state

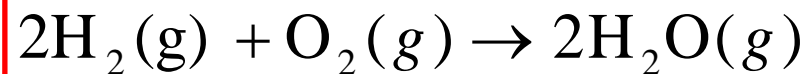


Final state

P_{ext}

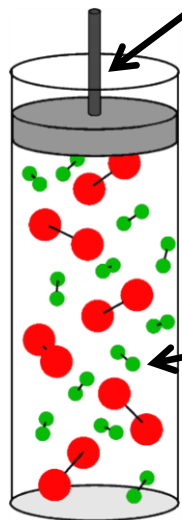
P_{ext}

Thermodynamics is about processes

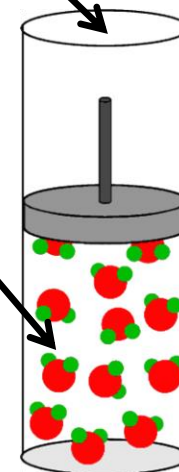
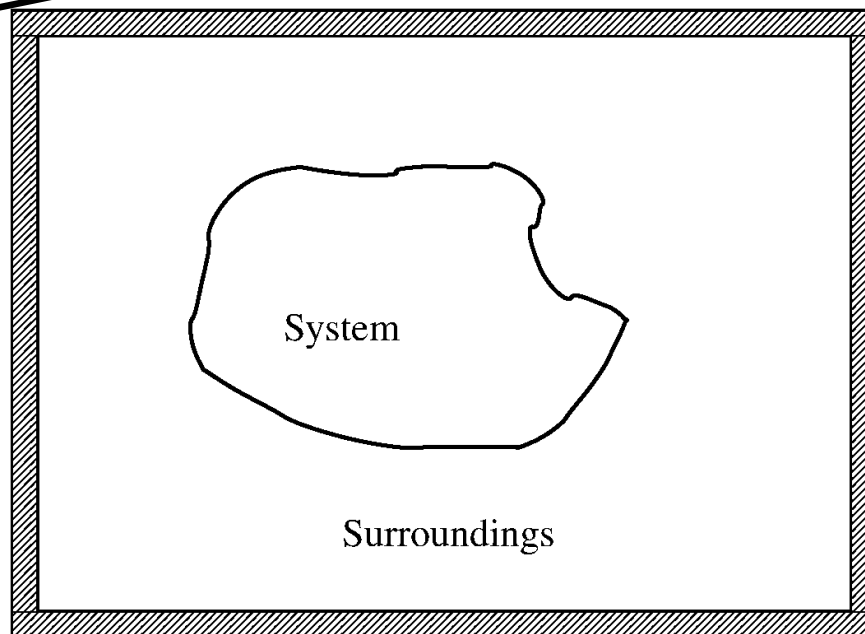


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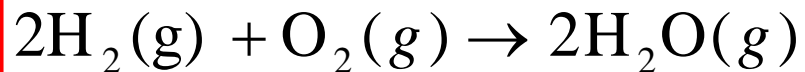


Initial state



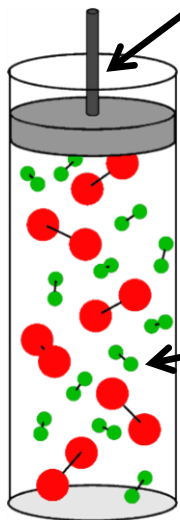
Final state

Thermodynamics is about processes

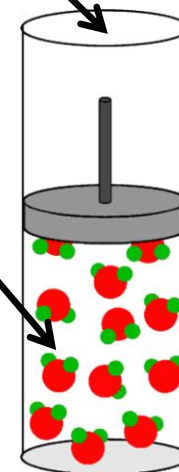
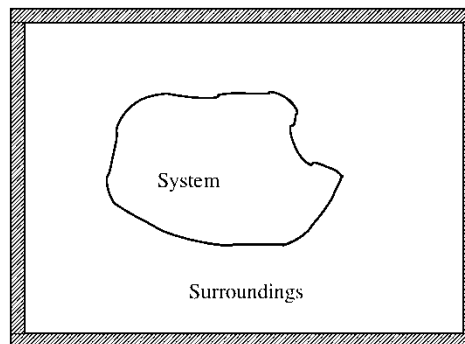


Some new definitions:

- Surroundings are external to the system:



Initial state

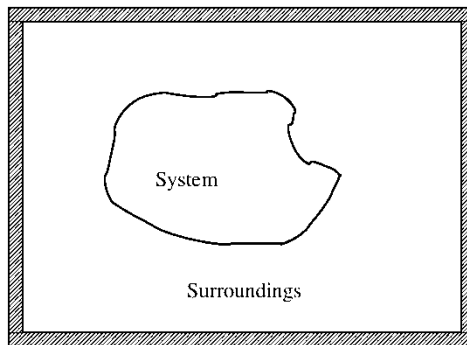
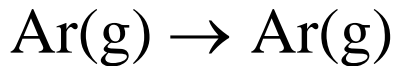


Final state

System

- P : Pressure
- T : Temperature
- V : Volume
- n : # moles

Thermodynamics is about processes



Equilibrium states

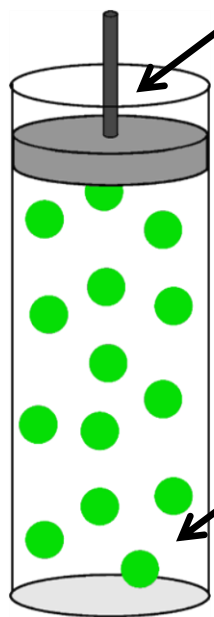
$$P_I = P_{\text{ext}}^I$$

$$P_F = P_{\text{ext}}^F$$

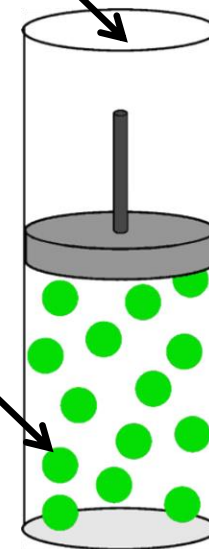
$$n_I = n_F$$

$$V_I \neq V_F$$

$$T_I = T_F$$

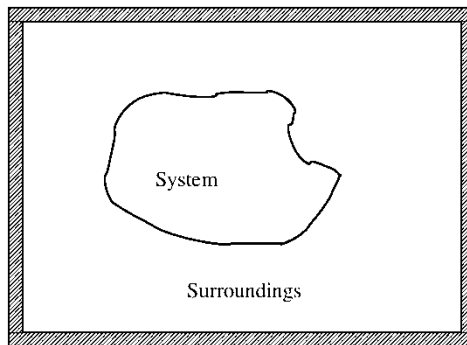
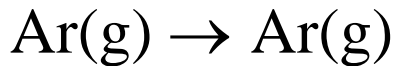


Initial state



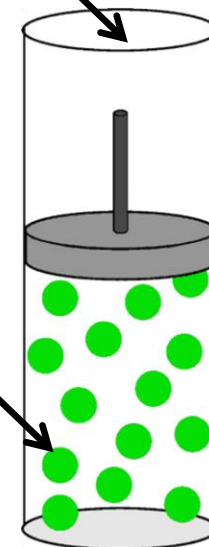
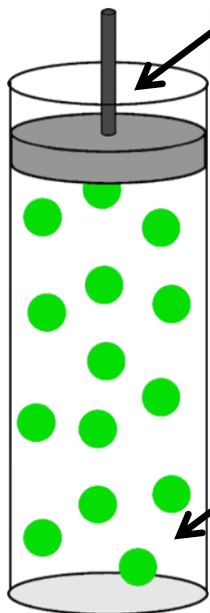
Final state

Thermodynamics is about processes



$$P_{\text{ext}}^{\text{I}}$$

$$P_{\text{ext}}^{\text{F}}$$



$$P_{\text{I}}$$

$$P_{\text{F}}$$

Equilibrium states

Initial state

Final state

Closed system

$$P_{\text{I}} = P_{\text{ext}}^{\text{I}}$$

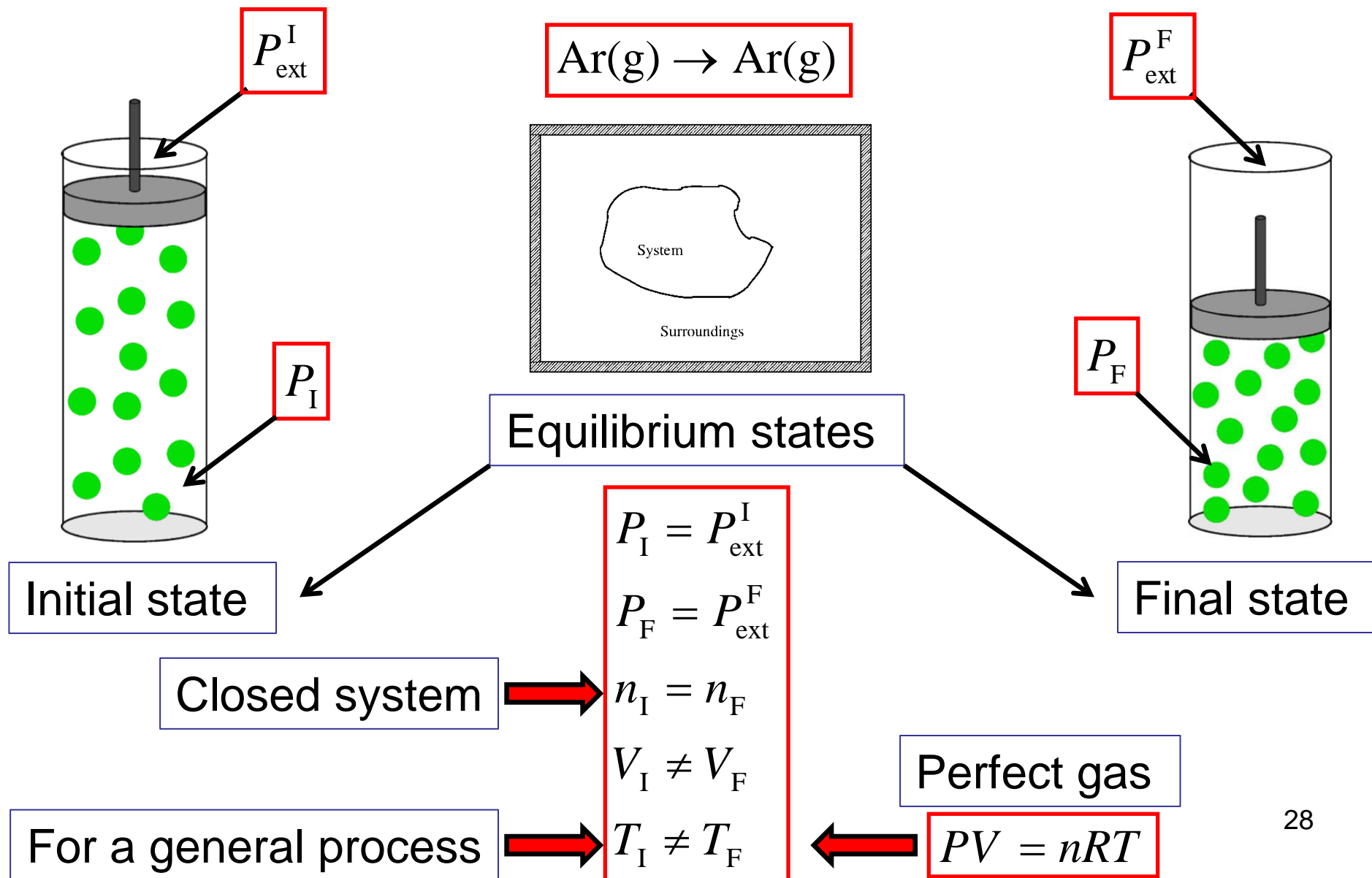
$$P_{\text{F}} = P_{\text{ext}}^{\text{F}}$$

$$n_{\text{I}} = n_{\text{F}}$$

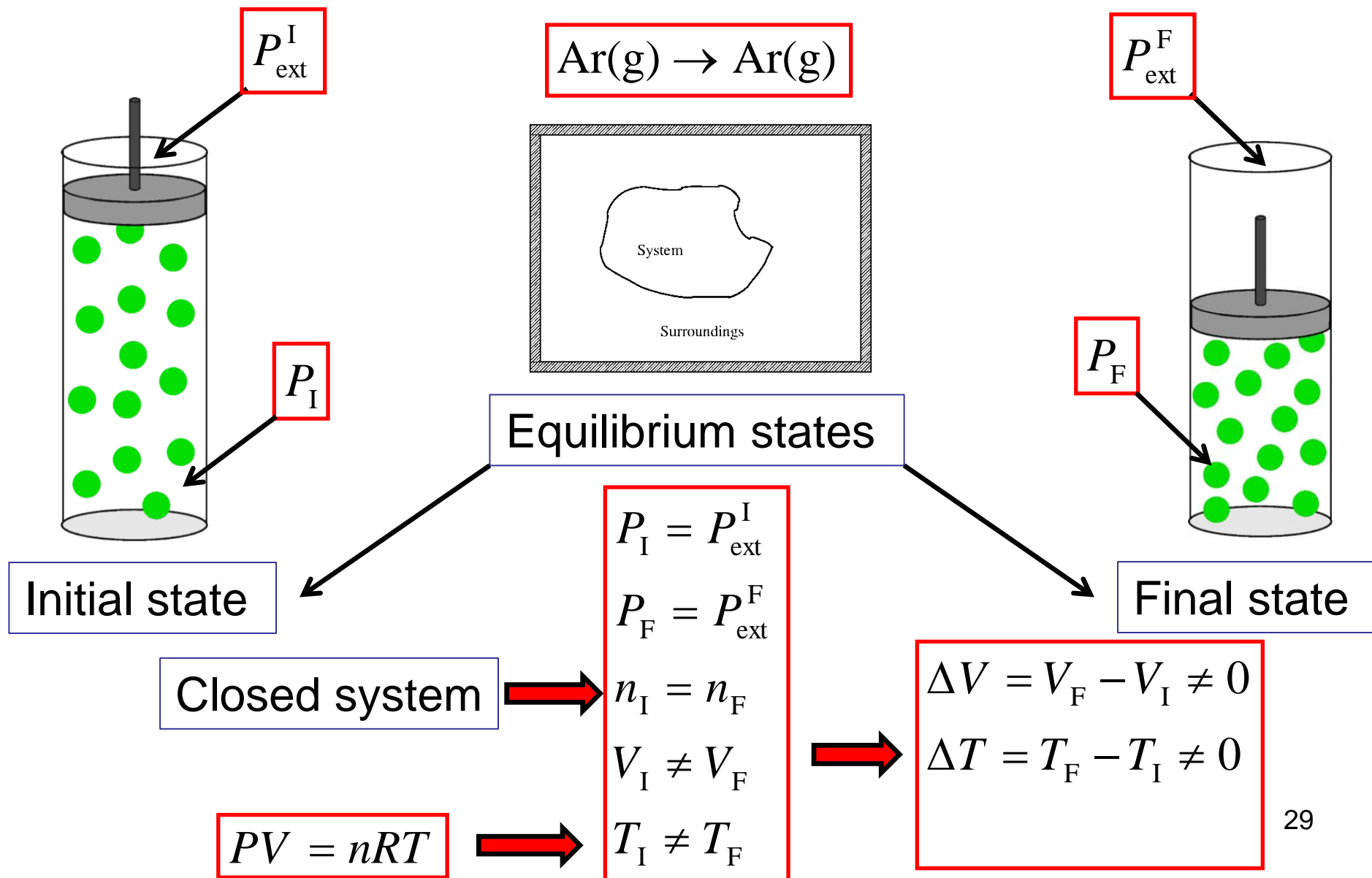
$$V_{\text{I}} \neq V_{\text{F}}$$

$$T_{\text{I}} = T_{\text{F}}$$

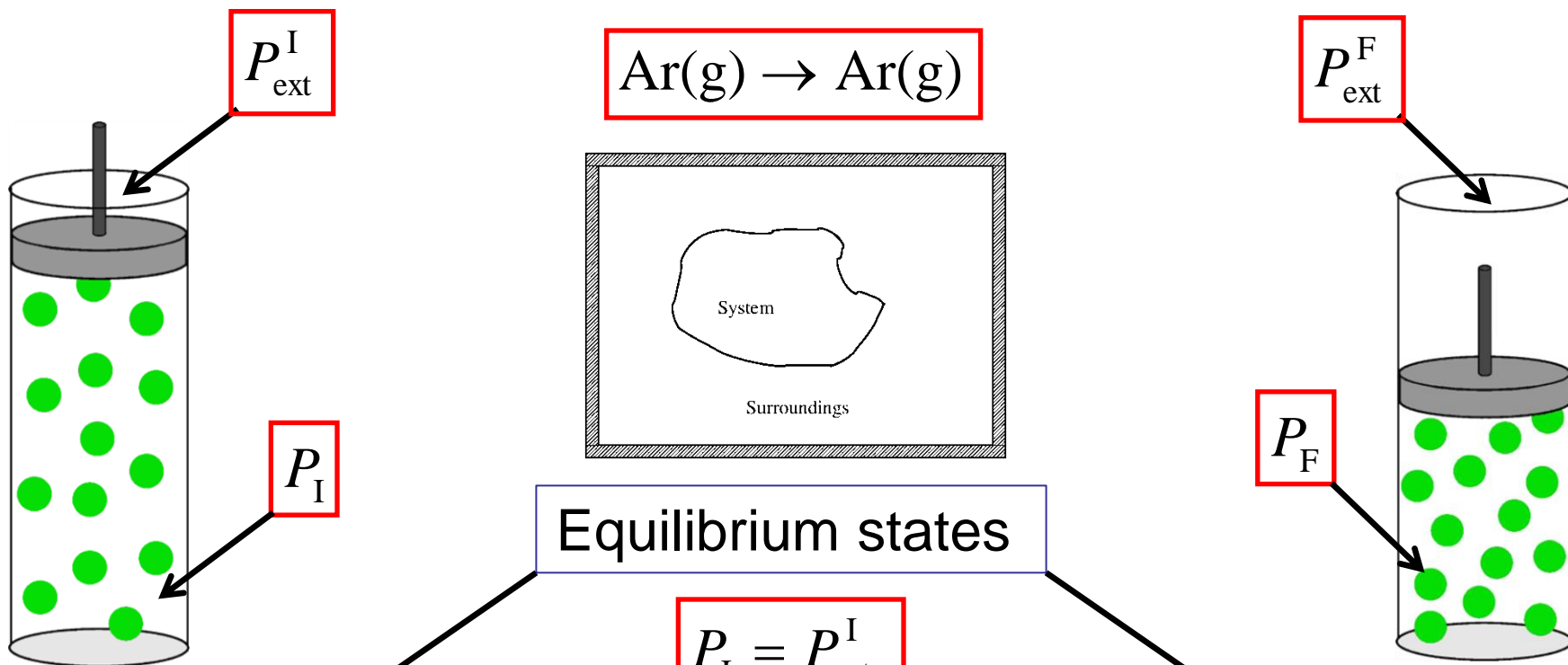
Thermodynamics is about processes



Thermodynamics is about processes



Thermodynamics is about processes



Initial state

Closed system

$$PV = nRT$$

$$P_{\text{I}} = P_{\text{ext}}^{\text{I}}$$

$$P_{\text{F}} = P_{\text{ext}}^{\text{F}}$$

$$n_{\text{I}} = n_{\text{F}}$$

$$V_{\text{I}} \neq V_{\text{F}}$$

$$T_{\text{I}} \neq T_{\text{F}}$$

$$\Delta V = V_{\text{F}} - V_{\text{I}} \neq 0$$

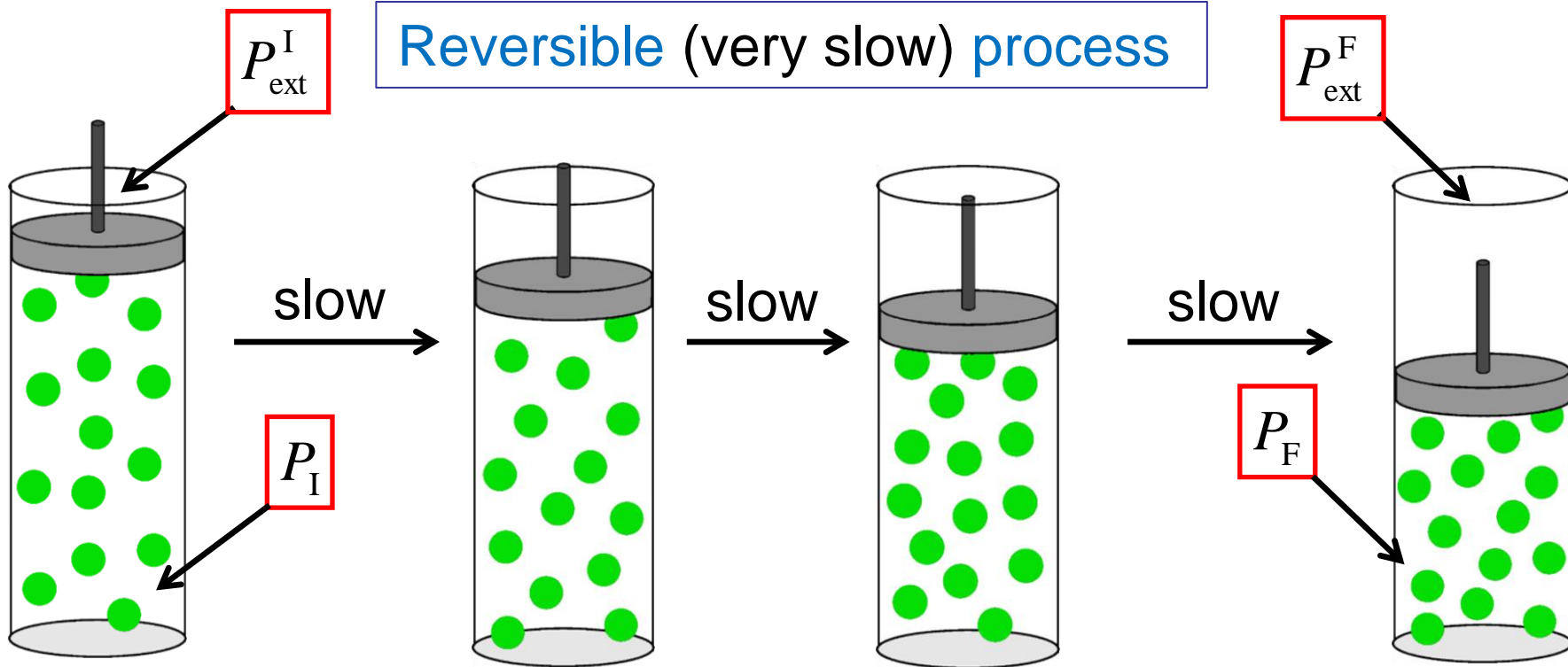
$$\Delta T = T_{\text{F}} - T_{\text{I}} \neq 0$$

$$\Delta P = P_{\text{F}} - P_{\text{I}} \neq 0$$

Final state

Thermodynamics is about processes

Reversible (very slow) process



Initial state

Intermediate states

Final state

$$P_I = P_{ext}^I$$

$$P_{intermediate} = P_{ext}$$

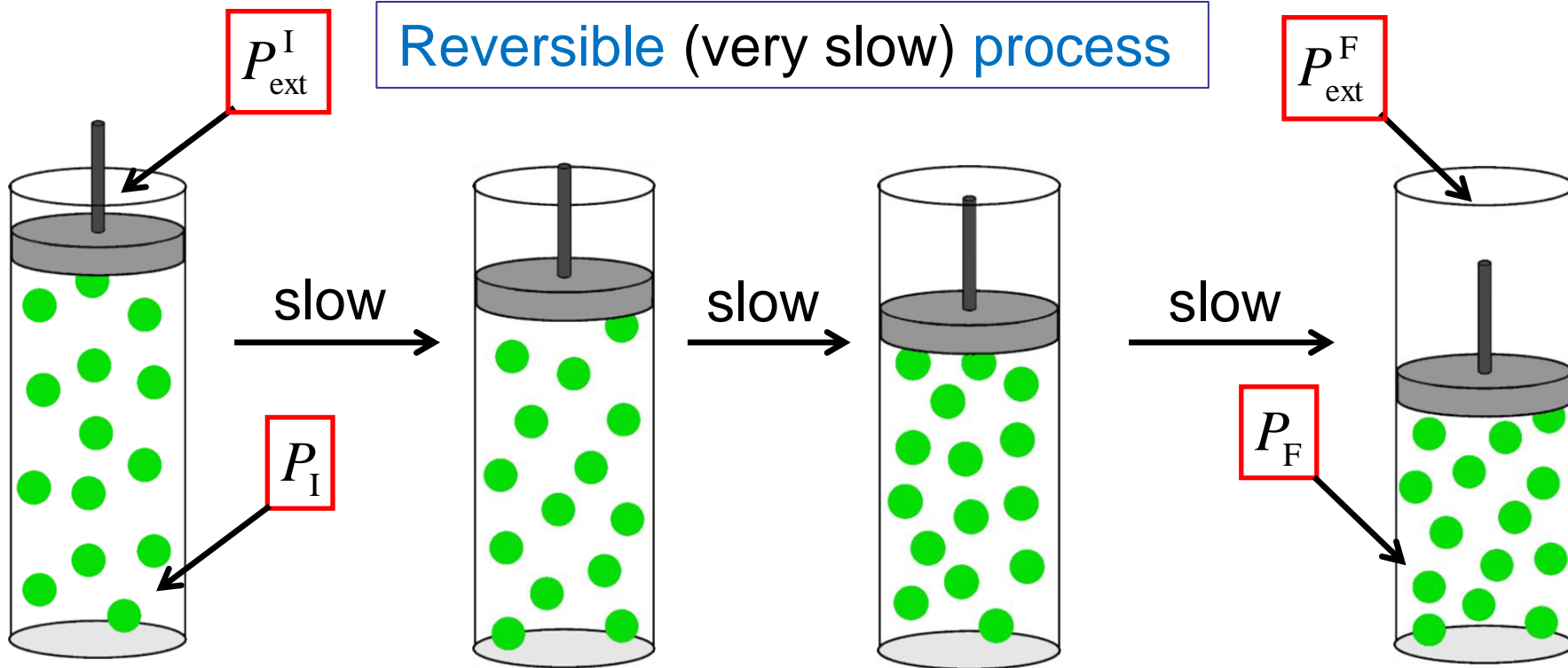
$$P_F = P_{ext}^F$$

Equilibrium

Equilibrium

Thermodynamics is about processes

Reversible (very slow) process



Initial state

Intermediate states

Final state

$$P_I = P_{\text{ext}}^I$$

$$P_{\text{intermediate}} = P_{\text{ext}}$$

$$P_F = P_{\text{ext}}^F$$

Equilibrium

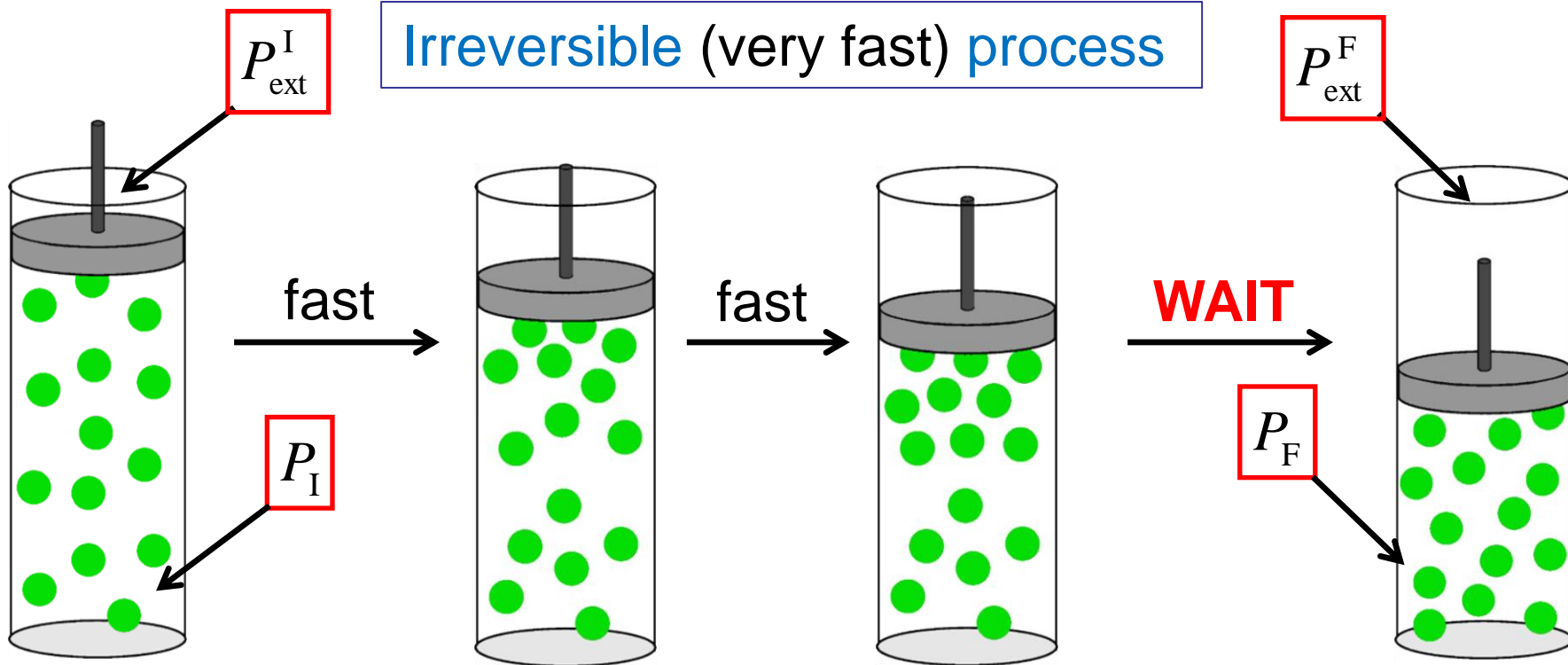
Equilibrium states

Equilibrium

Reversible process

Thermodynamics is about processes

Irreversible (very fast) process



Initial state

Intermediate states

Final state

$$P_{\text{I}} = P_{\text{ext}}^{\text{I}}$$

$$P_{\text{intermediate}} \neq P_{\text{ext}}$$

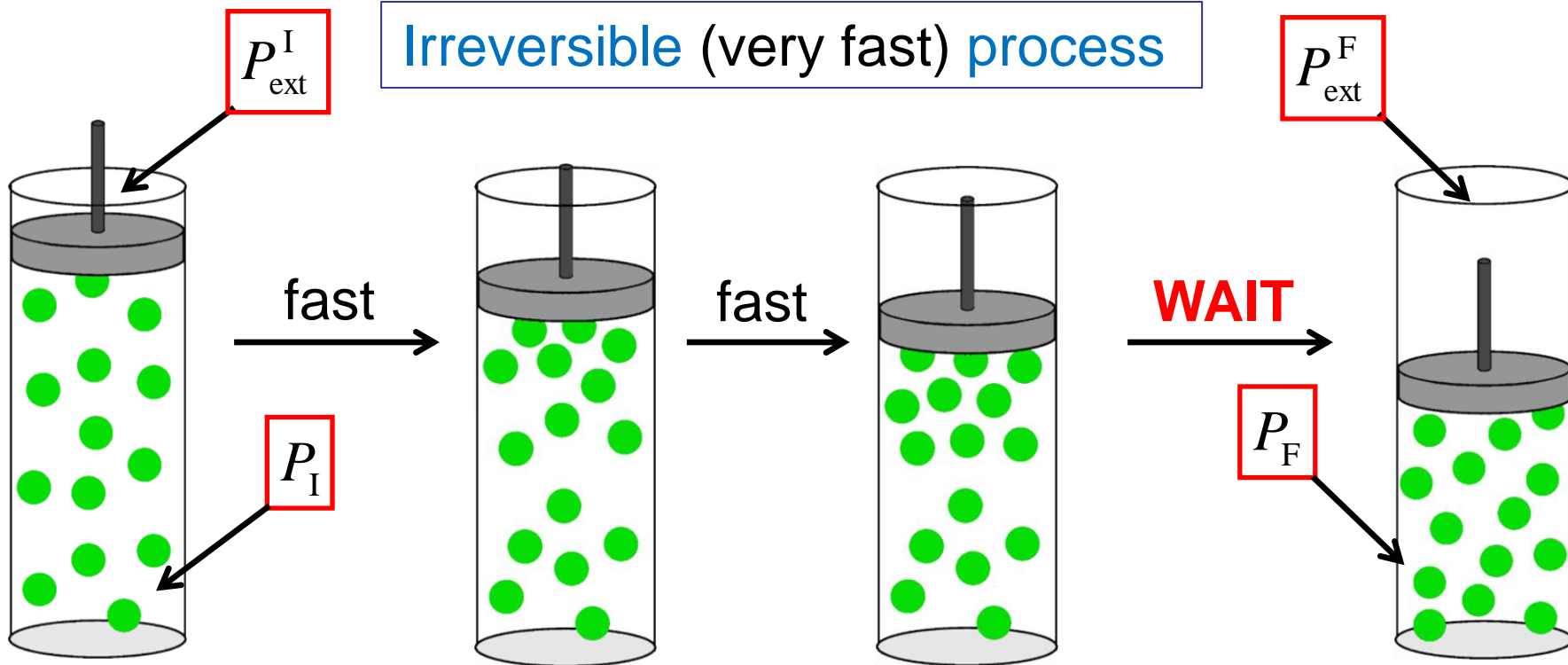
$$P_{\text{F}} = P_{\text{ext}}^{\text{F}}$$

Equilibrium

Equilibrium

Thermodynamics is about processes

Irreversible (very fast) process



Initial state

Intermediate states

Final state

$$P_I = P_{ext}^I$$

$$P_{intermediate} \neq P_{ext}$$

$$P_F = P_{ext}^F$$

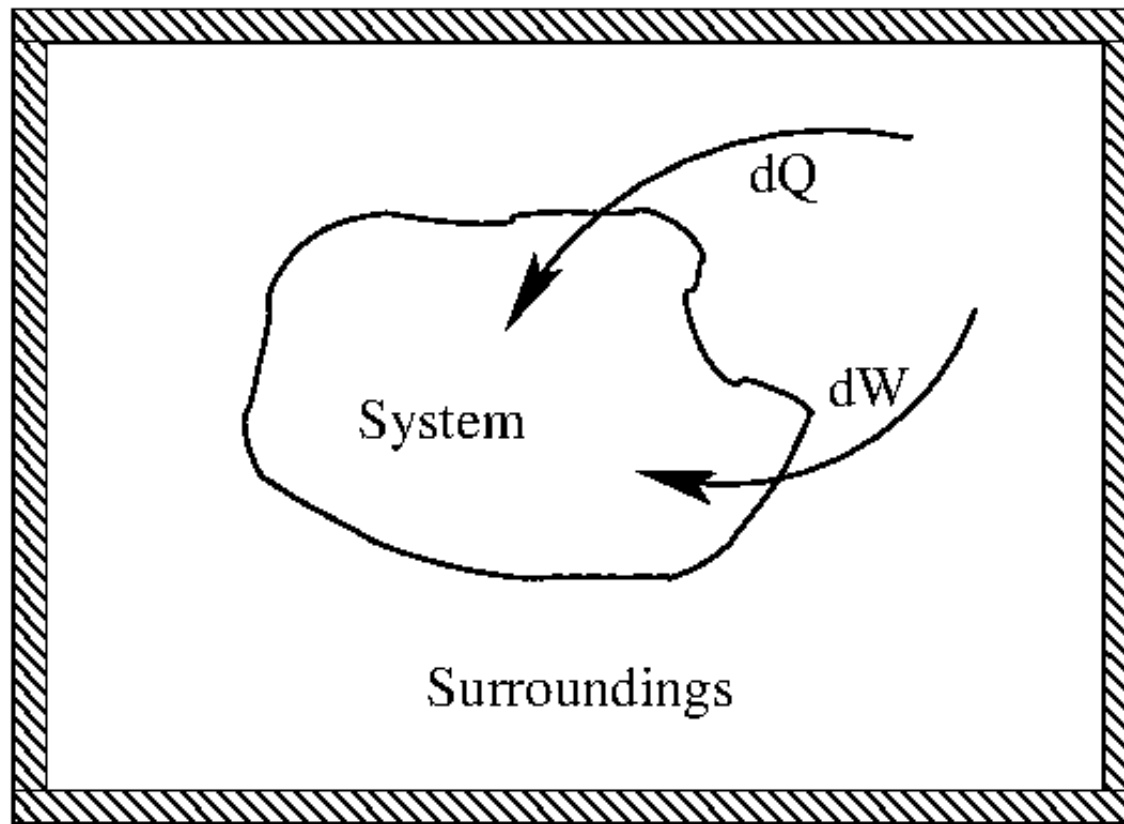
Equilibrium

NON-equilibrium states

Equilibrium

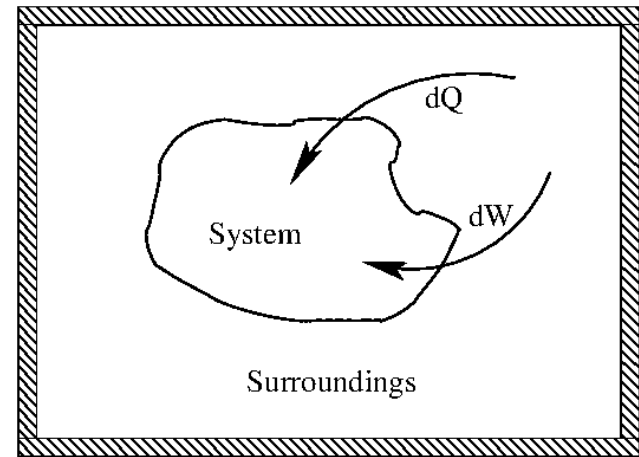
Irreversible process

Thermodynamics is about processes
both reversible and irreversible processes



Thermodynamics is based on two laws

These laws are
phenomenological



- First law: conservation of energy

$$dU = dW + dQ$$

- U : internal energy of the system
- Q : the heat in the process
- W : the work in the process
(any other form of energy involved in the process)

- Second law: for any spontaneous process

$$dS_{\text{tot}} = dS + dS_{\text{sur}} \geq 0$$

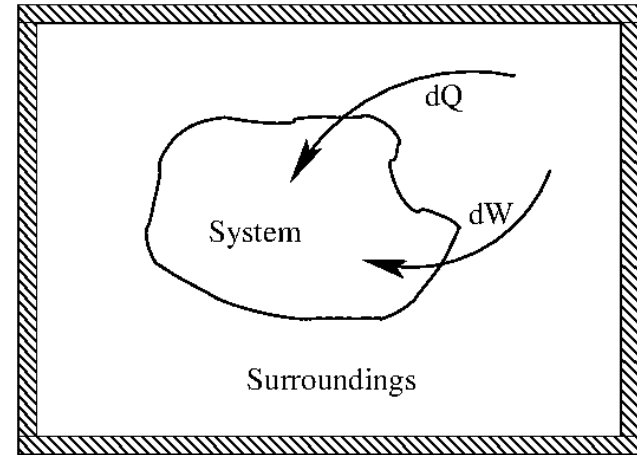
- S : entropy of the system
- S : related to the heat Q and T

Thermodynamics: First law

- First law: conservation of energy

$$dU = dW + dQ$$

- U : internal energy of the system
- Q : the heat in the process
- W : the work in the process
(any other form of energy involved in the process)

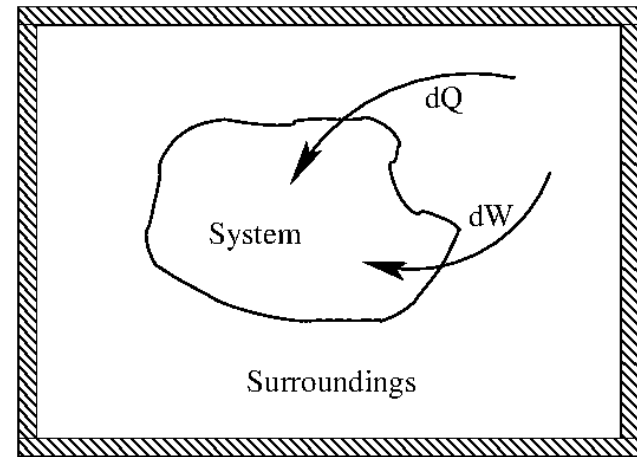


Thermodynamics: First law

- First law: conservation of energy

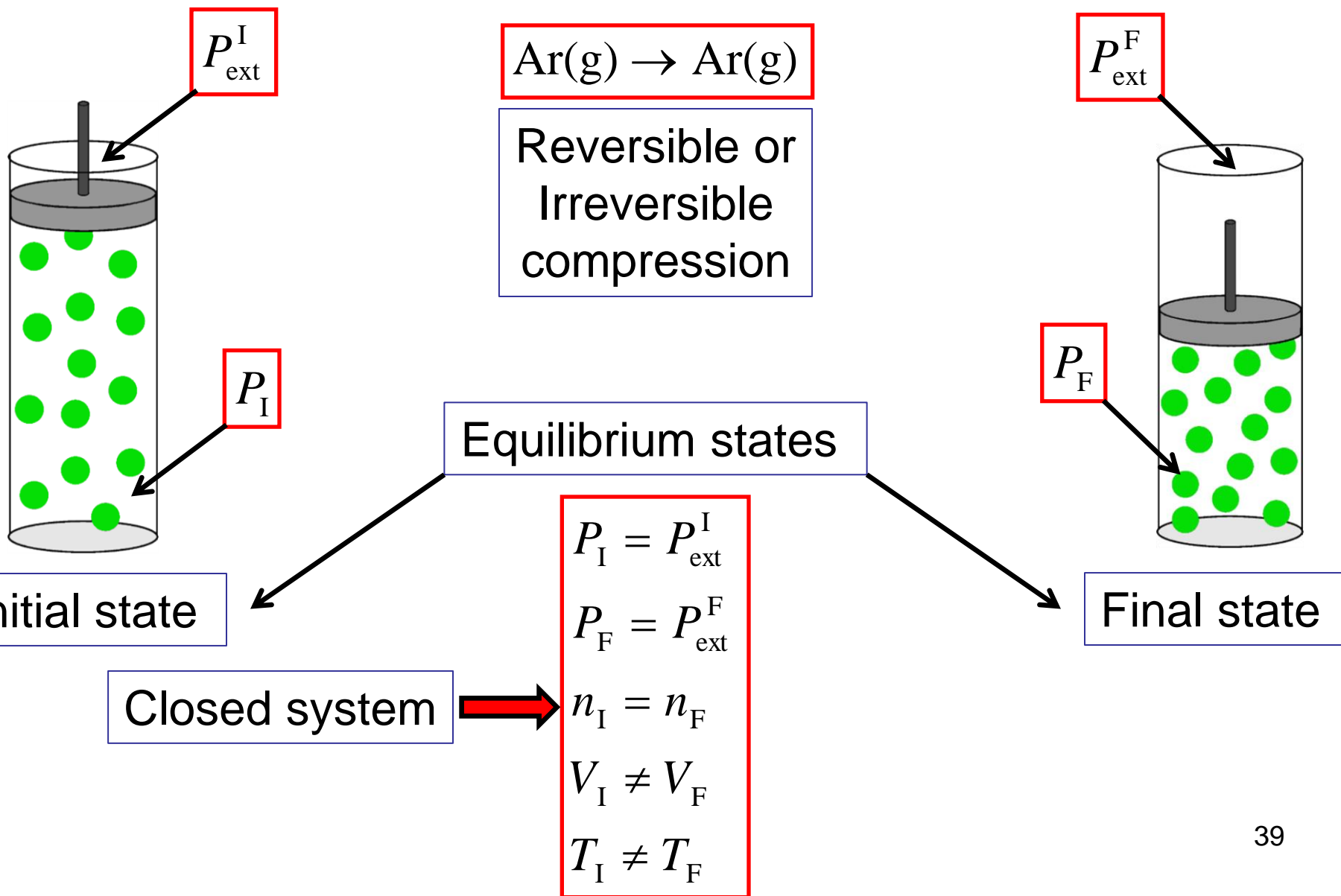
$$dU = dW + dQ$$

- U : internal energy of the system
- Q : the heat in the process
- W : the work in the process
(any other form of energy involved in the process)

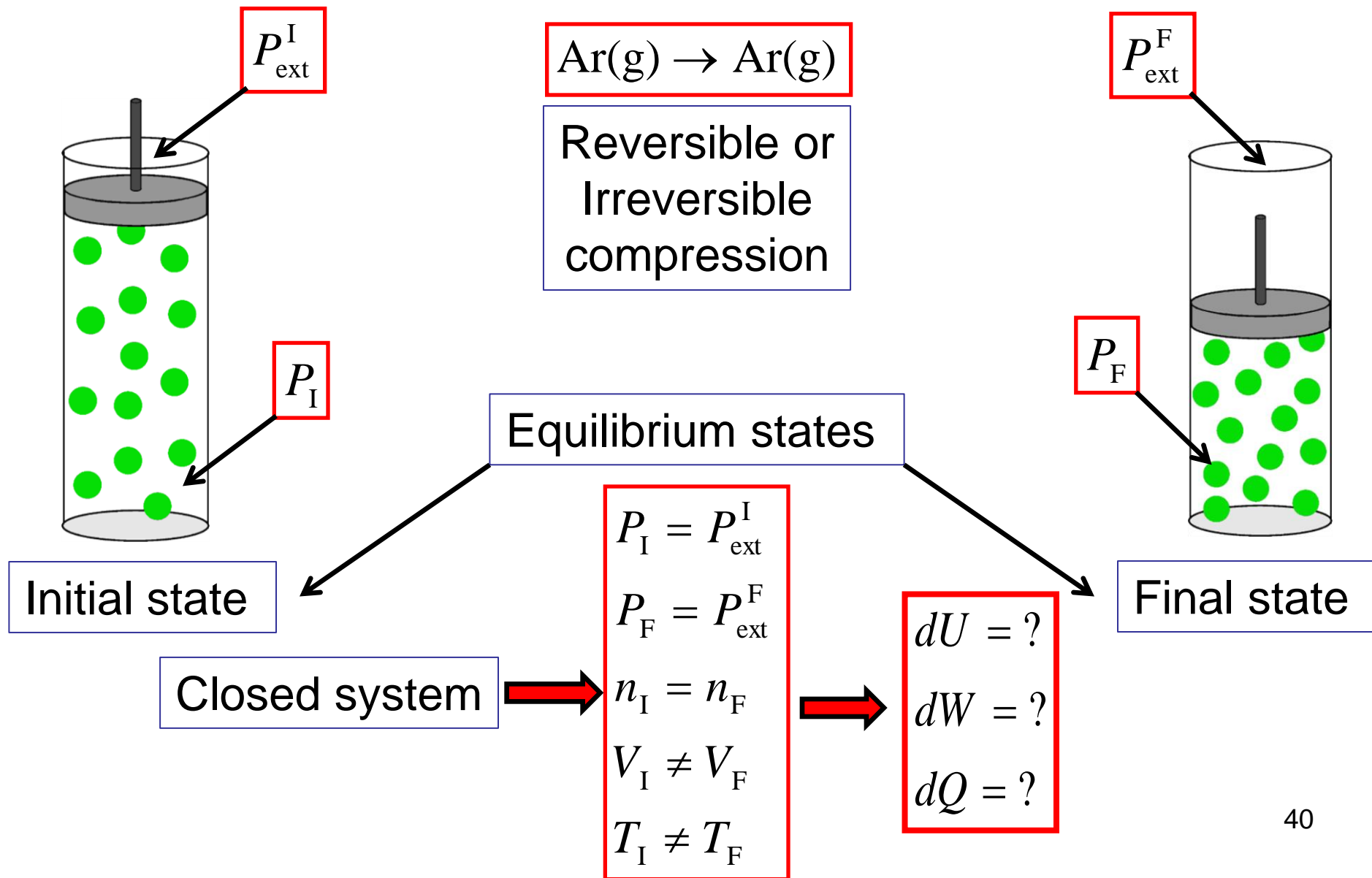


- dU : infinitesimally small change of internal energy of the system
- dQ : infinitesimally small change of the heat in the process
- dW : infinitesimally small change of the work in the process

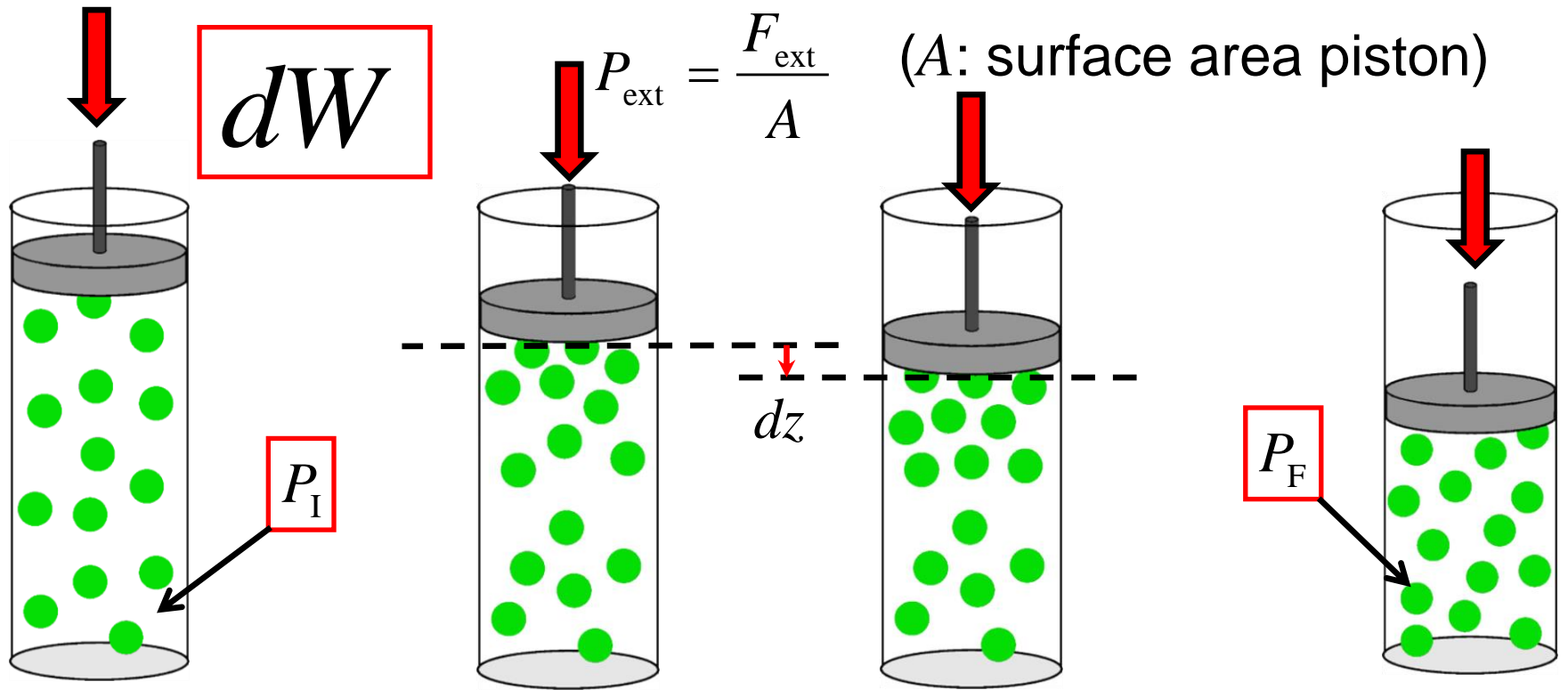
Thermodynamics: First law: Example



Thermodynamics: First law: Example



Thermodynamics: First law: Example

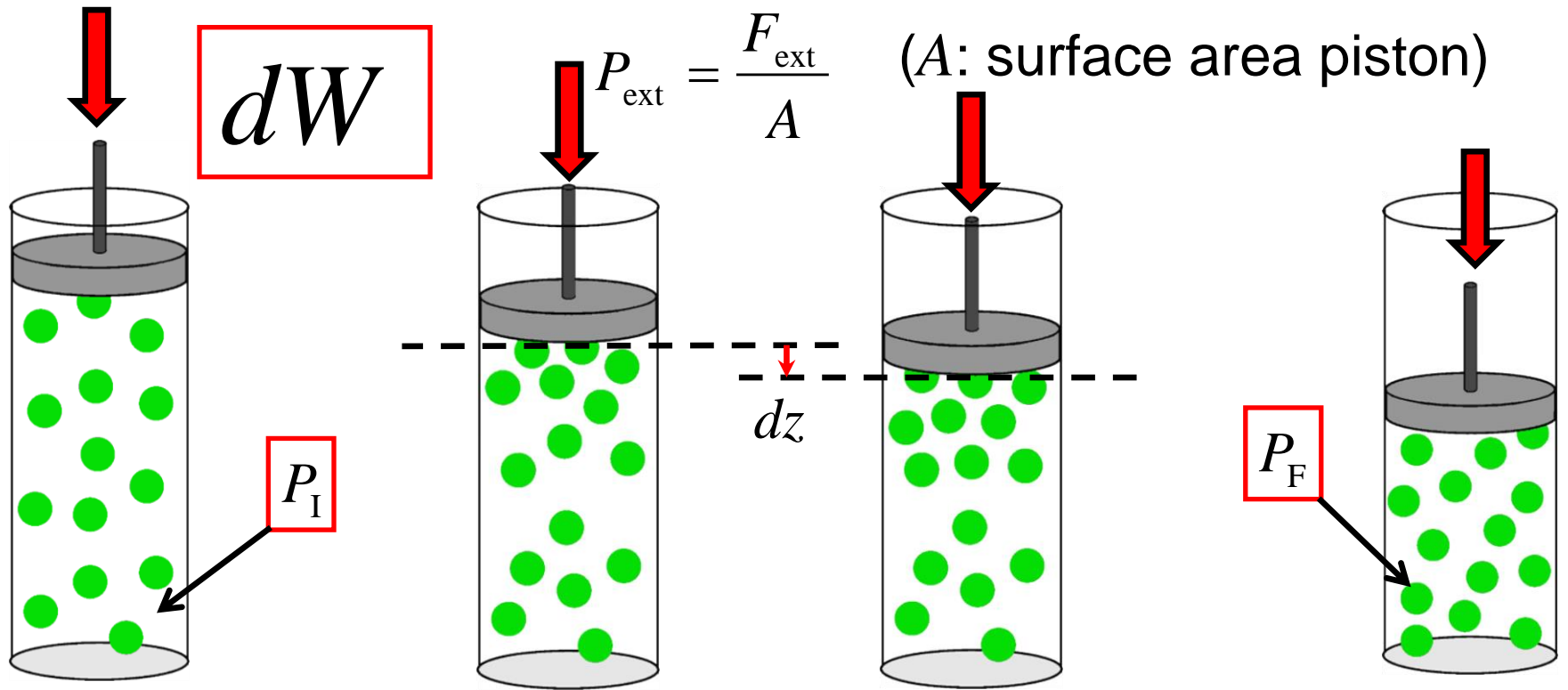


Initial state

$$dW = F_{\text{ext}} dz = P_{\text{ext}} Adz = -P_{\text{ext}} dV$$

Final state

Thermodynamics: First law: Example

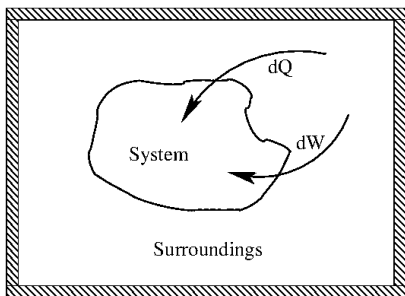


Initial state

Final state

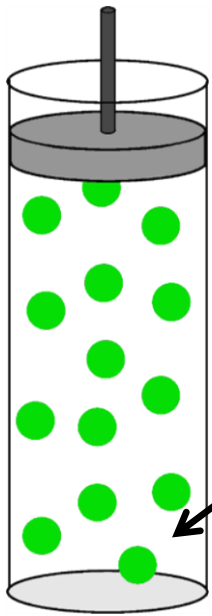
$$dW = F_{\text{ext}} dz = P_{\text{ext}} Adz = -P_{\text{ext}} dV$$

$dW > 0$ for compression ($dV < 0$)
“W is the work done on the system”

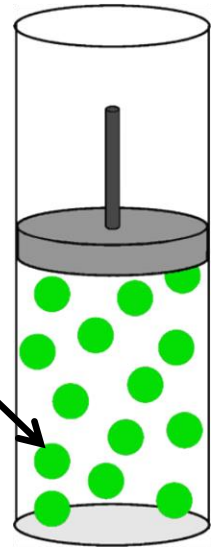
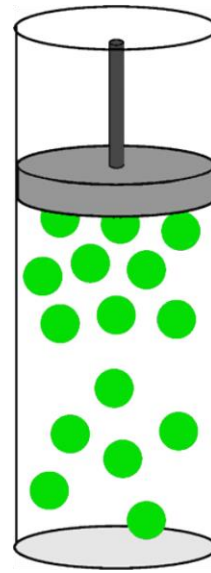
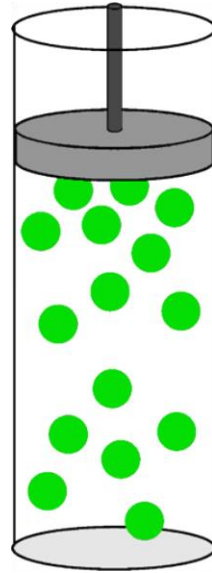


Thermodynamics: First law: Example

$$dQ$$



$$P_I$$



$$P_F$$

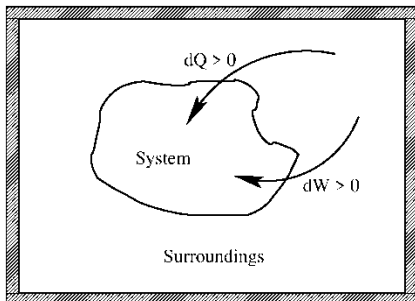
Initial state

Final state

$$dU = dQ + dW$$



$$dQ = dU - dW$$

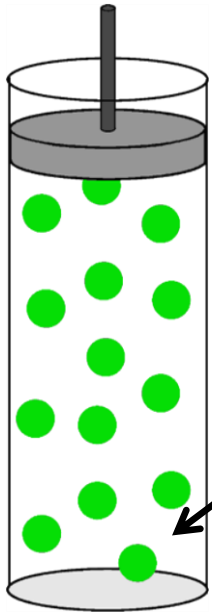


$dQ > 0$ for heat entering the system
“ dQ is related to the entropy S and T ”

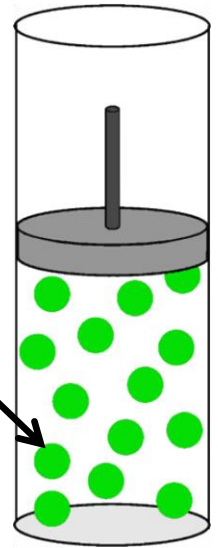
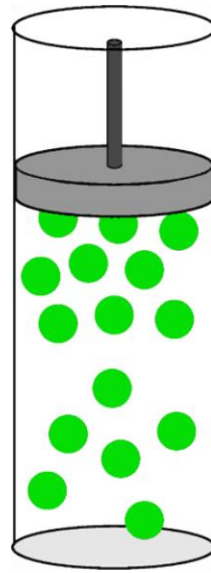
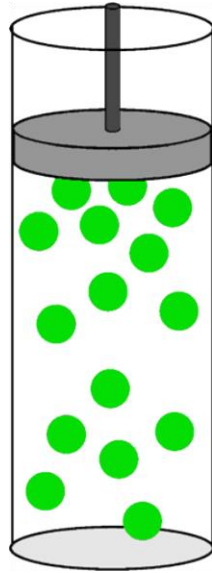
Thermodynamics: First law: Example

$$dU$$

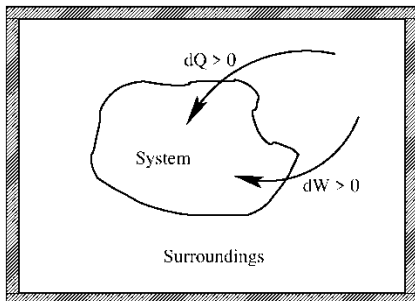
To find dU for a general system we need dQ and dW and the first law

 P_I

Initial state

 P_F

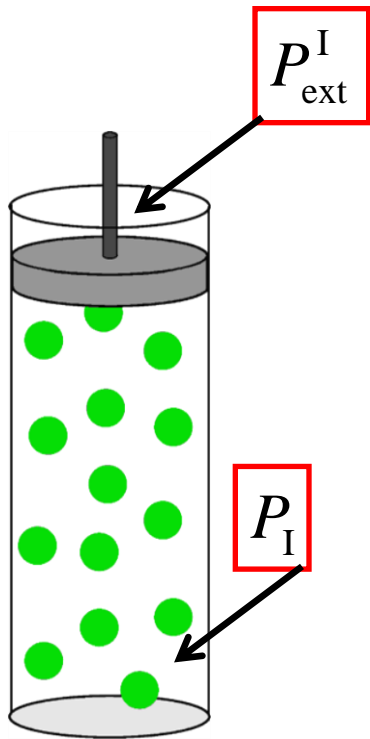
Final state



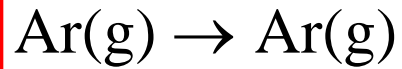
For a perfect gas of atoms
(see page 4-5 Study Guide)

$$U = \frac{3}{2} nRT$$

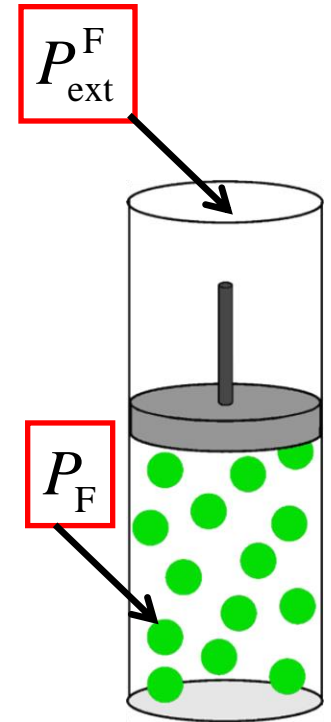
Thermodynamics: First law: Example



Initial state



Reversible or
Irreversible
compression



Final state

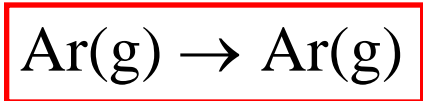
Equilibrium states

$$\Delta U = U^{\text{state F}} - U^{\text{state I}} = \int_{\text{state I}}^{\text{state F}} dU$$

$$\Delta W \equiv W = \int_{\text{state I}}^{\text{state F}} dW$$

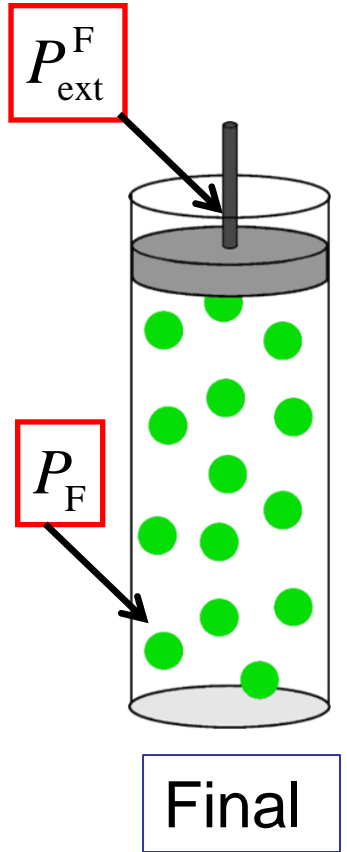
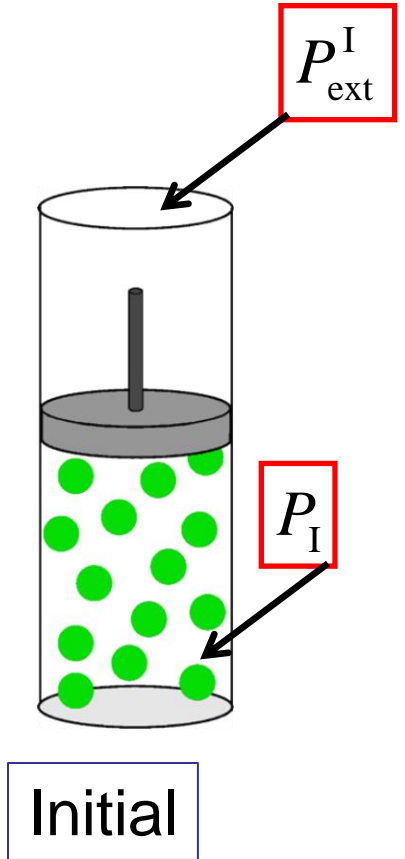
$$\Delta Q \equiv Q = \int_{\text{state I}}^{\text{state F}} dQ$$

Thermodynamics: Another example



$n = 3$
 $T_I = 300 \text{ K}$
 $P_I = 2 \text{ bar}$
 $P_F = 1 \text{ bar}$
 $V_F = 2V_I$

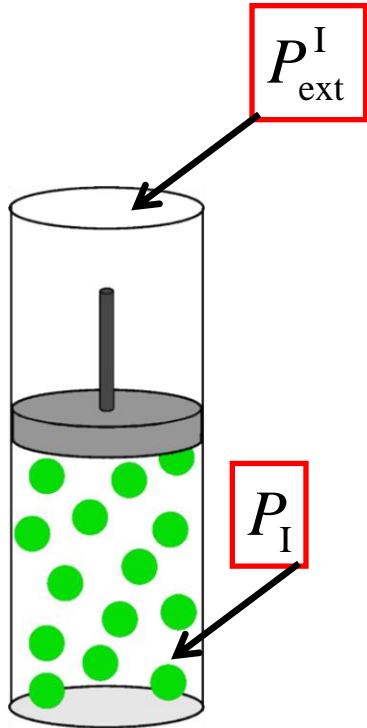
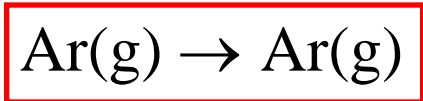
Reversible or irreversible
isothermal
expansion
of a
perfect gas



isothermal: constant temperature

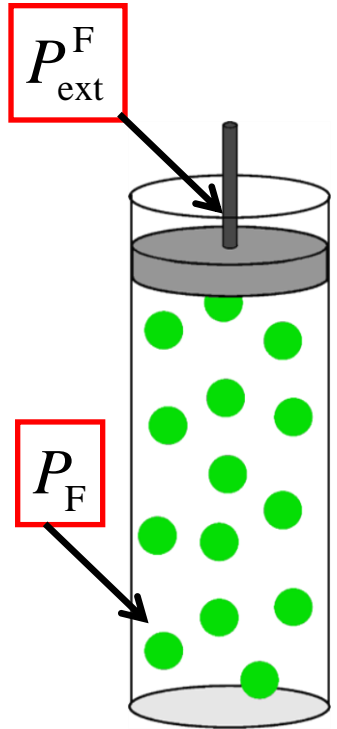
$dT = 0$

Thermodynamics: Another example



$n = 3$
 $T_I = 300 \text{ K}$
 $P_I = 2 \text{ bar}$
 $P_F = 1 \text{ bar}$
 $V_F = 2V_I$

Reversible or irreversible
isothermal
expansion
of a
perfect gas



Initial

Final

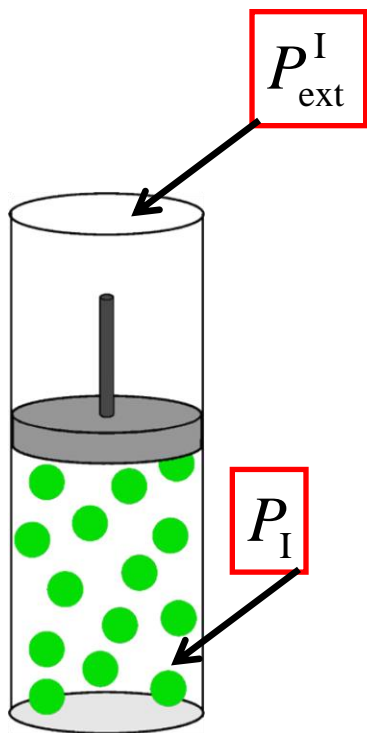
Isothermal: constant temperature

$dT = 0$

Closed system: constant amount

$dn = 0$

Thermodynamics: Another example



$$n = 3$$

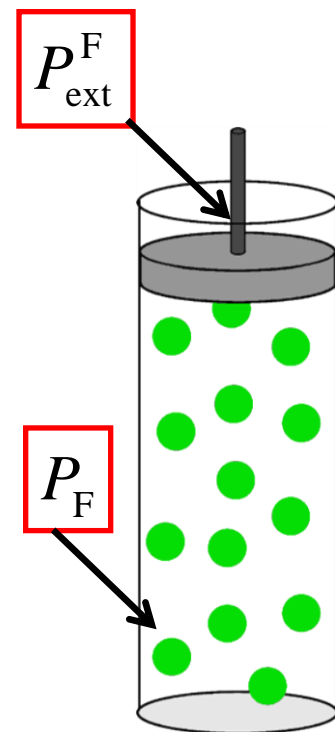
$$T_{\text{I}} = 300 \text{ K}$$

$$P_{\text{I}} = 2 \text{ bar}$$

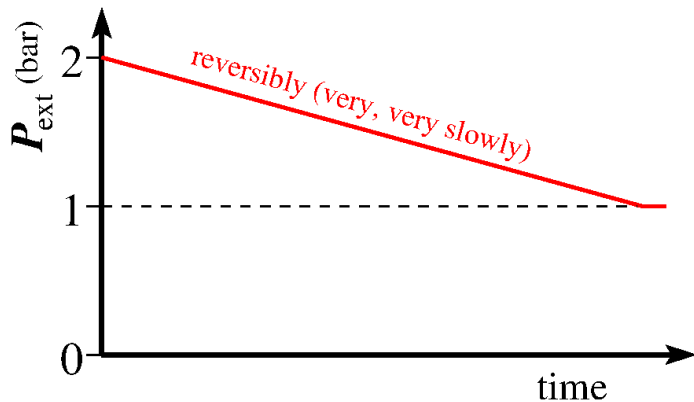
$$P_{\text{F}} = 1 \text{ bar}$$

$$V_{\text{F}} = 2V_{\text{I}}$$

Reversible or
irreversible
isothermal
expansion
of a
perfect gas

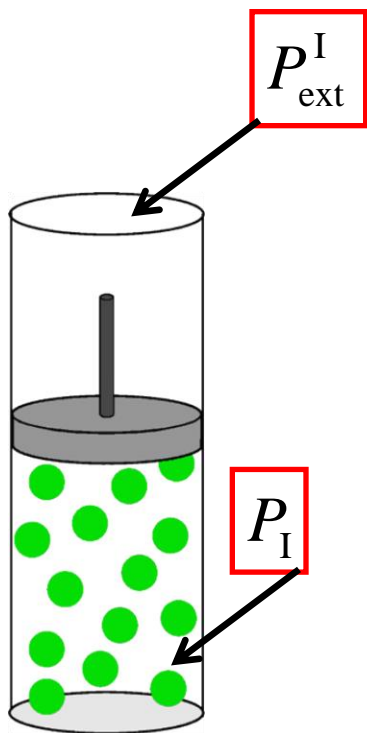
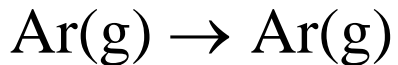


Initial



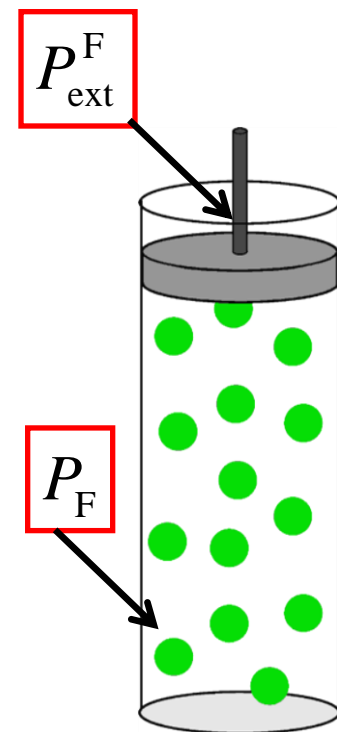
Final

Thermodynamics: Another example

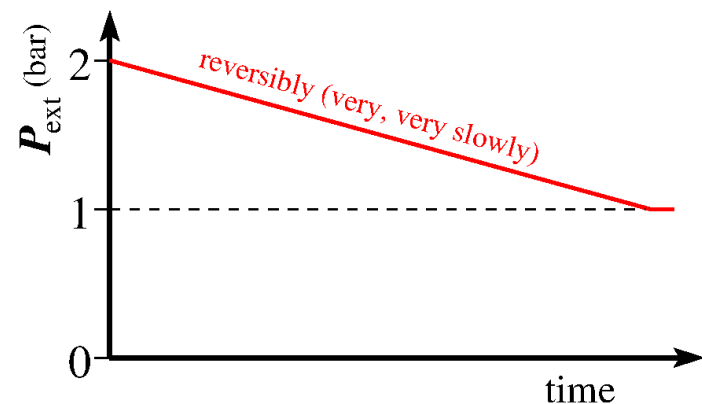


$$\begin{aligned} n &= 3 \\ T_{\text{I}} &= 300 \text{ K} \\ P_{\text{I}} &= 2 \text{ bar} \\ P_{\text{F}} &= 1 \text{ bar} \\ V_{\text{F}} &= 2V_{\text{I}} \end{aligned}$$

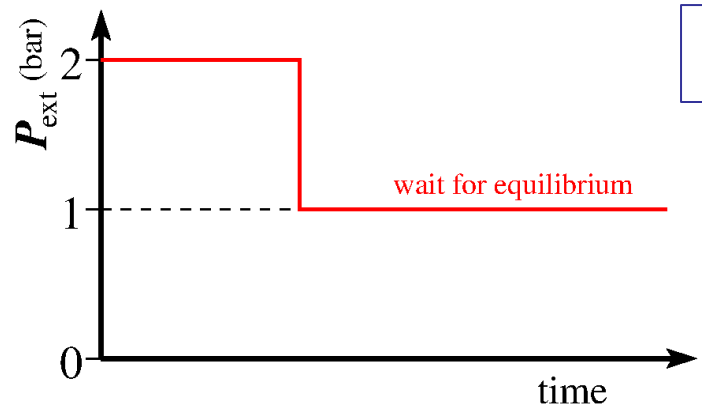
Reversible or irreversible
isothermal
expansion
of a
perfect gas



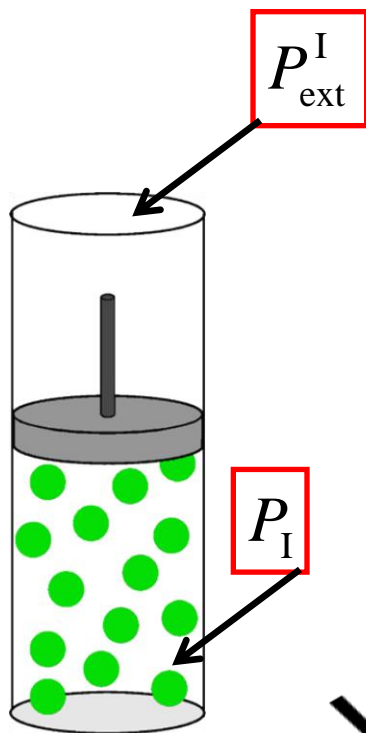
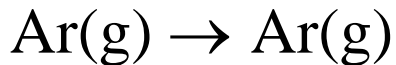
Initial



Final

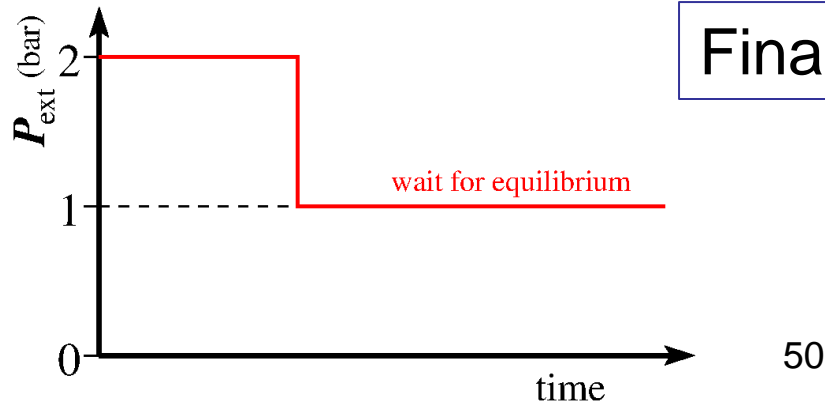
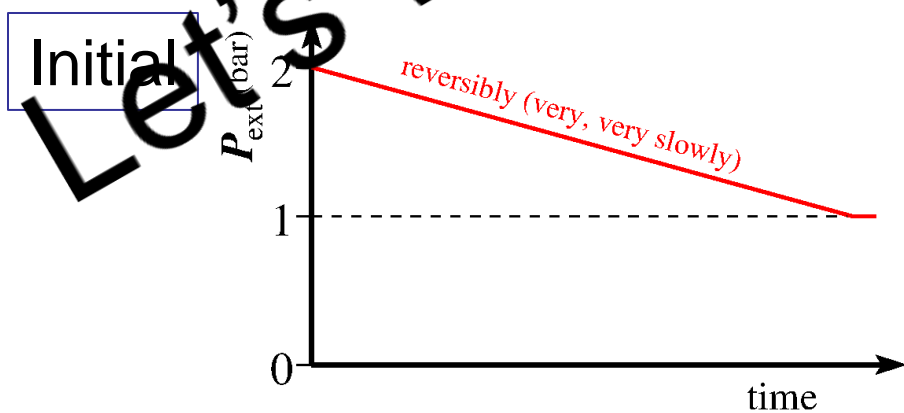
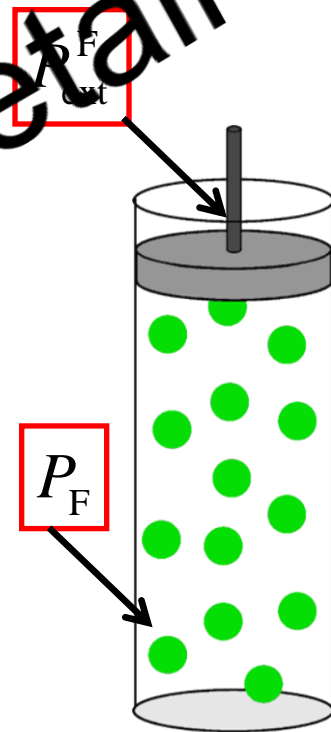


Thermodynamics: Another example



$n = 3$
 $T_I = 300 \text{ K}$
 $P_I = 2 \text{ bar}$
 $P_F = 1 \text{ bar}$
 $V_F = 2V_I$

Reversible or irreversible
isothermal
expansion
of a
perfect gas



Let's work this out in detail

Conditional processes

Closed system

$$dn = 0$$

Isolated system

$$dn = dQ = 0$$

Isothermal process

$$dT = 0$$

Isobaric process

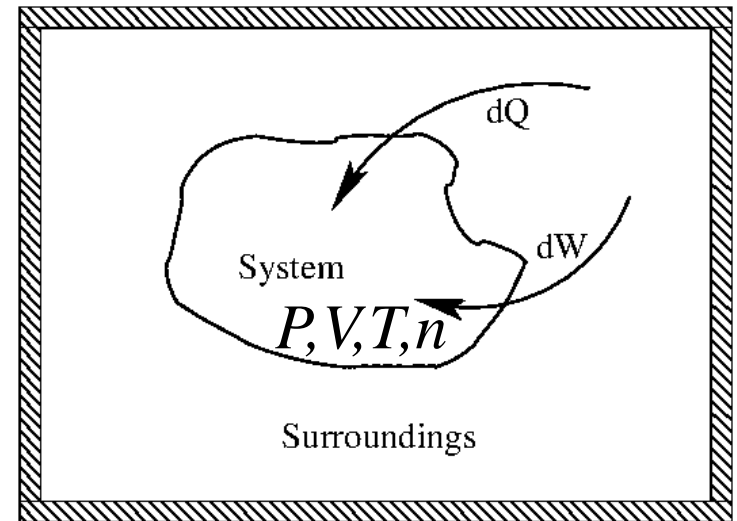
$$dP = 0$$

Isochoric process

$$dV = 0$$

Adiabatic process

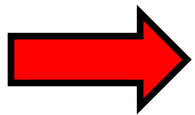
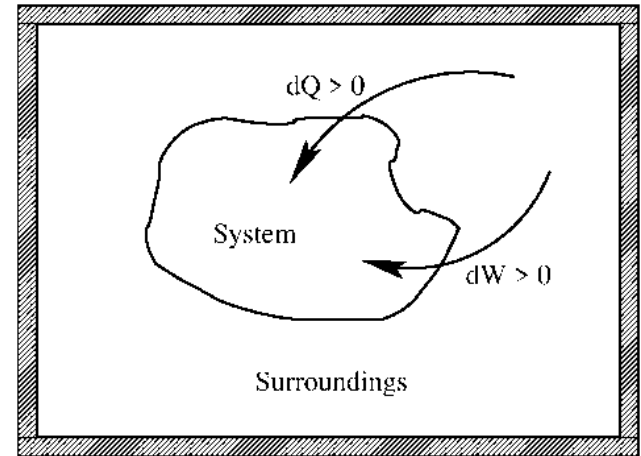
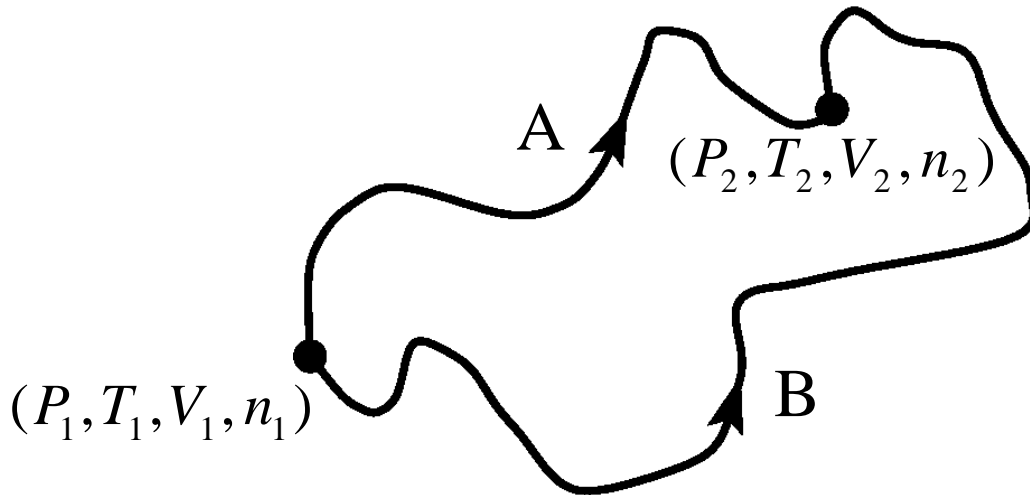
$$dQ = 0$$



Thermodynamics: First law

- First law: **conservation of energy**

$$dU = dW + dQ$$

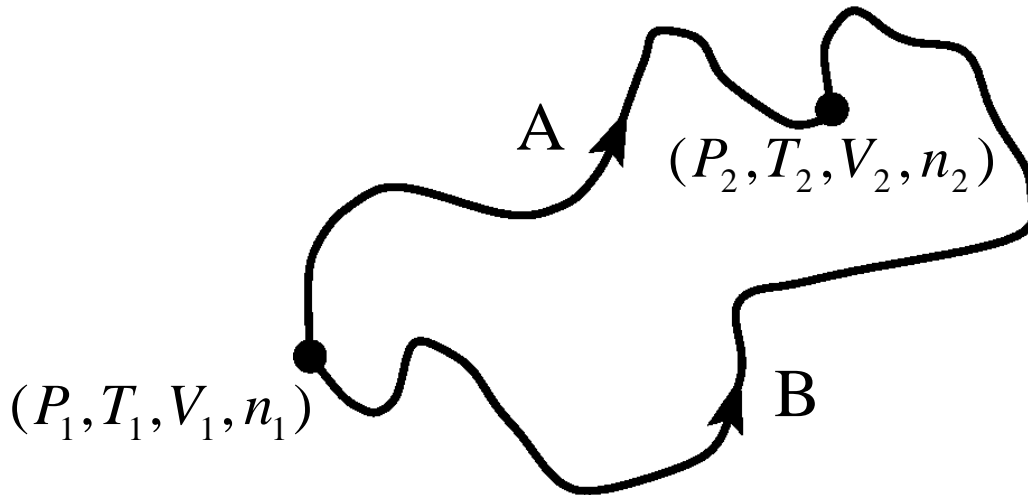
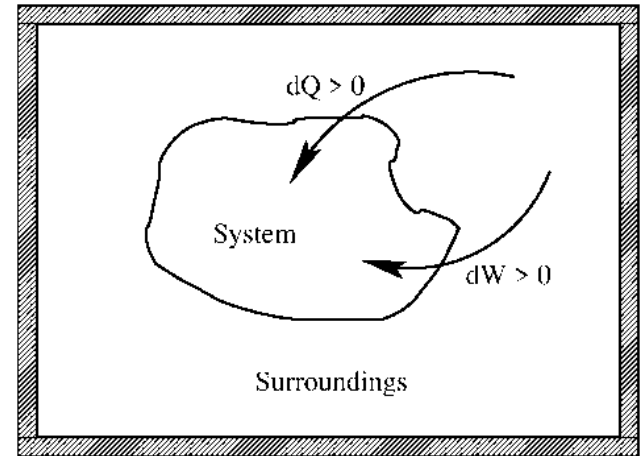


$$\Delta_A U = \int_{P_1, V_1, T_1, n_1}^{P_2, V_2, T_2, n_2} dU$$

Thermodynamics: First law

- First law: **conservation of energy**

$$dU = dW + dQ$$



According to first law:
 U is a state function:
a unique function
of the state variables

→

$$\Delta_A U = \int_{P_1, V_1, T_1, n_1}^{P_2, V_2, T_2, n_2} dU$$

however:

$$U = U(P, T, V, n)$$

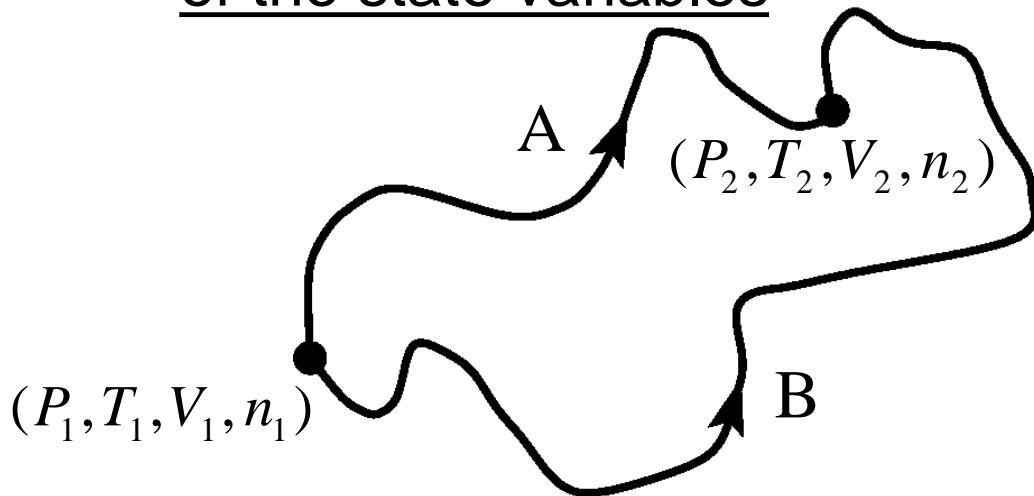
Thermodynamics: First law

- First law: **conservation of energy**

$$dU = dW + dQ$$

U is a unique function
of the state variables

$$U = U(P, T, V, n)$$



$$\left. \begin{aligned} \Delta_A U &= U(P_2, T_2, V_2, n_2) - U(P_1, T_1, V_1, n_1) \\ \Delta_B U &= U(P_2, T_2, V_2, n_2) - U(P_1, T_1, V_1, n_1) \end{aligned} \right\}$$

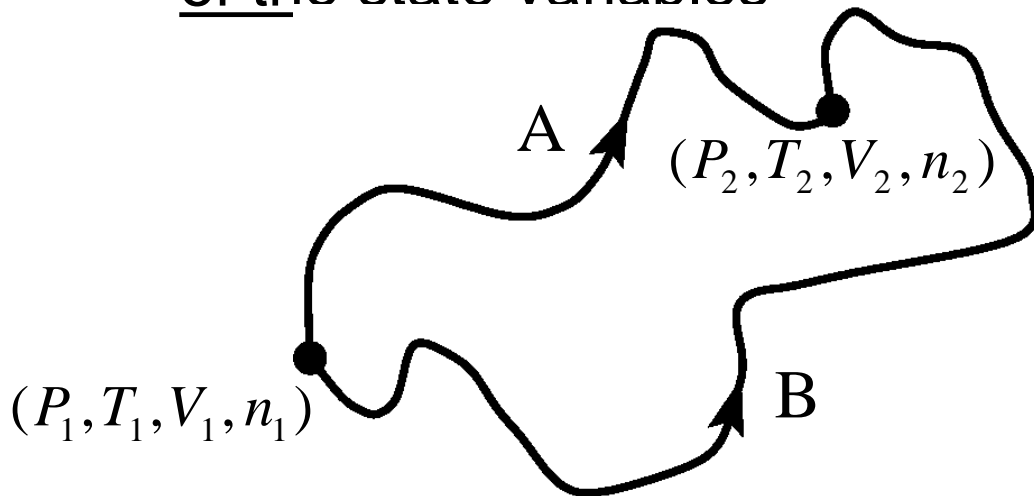
Thermodynamics: First law

- First law: **conservation of energy**

$$dU = dW + dQ$$

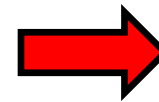
U is a unique function of the state variables

$$U = U(P, T, V, n)$$



$$\Delta_A U = U(P_2, T_2, V_2, n_2) - U(P_1, T_1, V_1, n_1)$$

$$\Delta_B U = U(P_2, T_2, V_2, n_2) - U(P_1, T_1, V_1, n_1)$$



$$\Delta_A U = \Delta_B U$$

ΔU is independent of path, whether reversible or irreversible

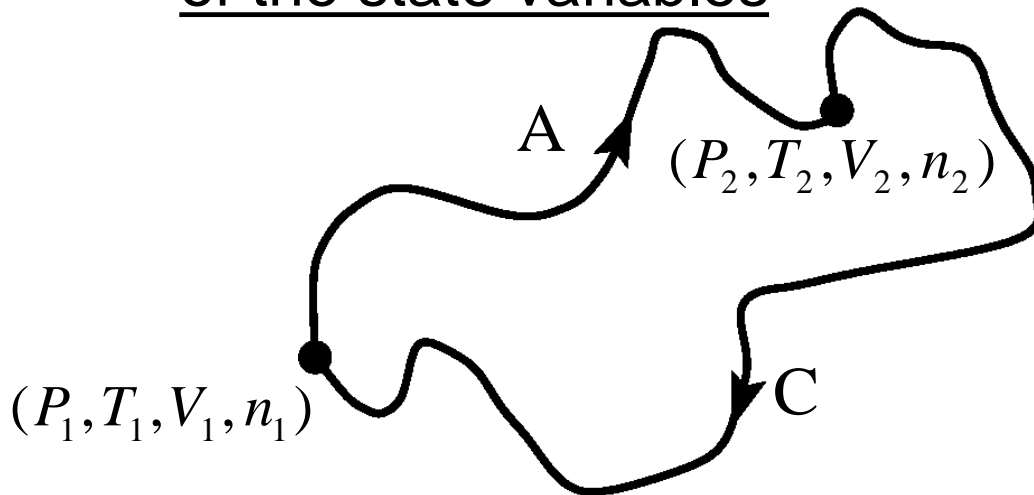
Thermodynamics: First law

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$$dU = dW + dQ$$

U is a unique function of the state variables

$$U = U(P, T, V, n)$$



Note the different directions for paths B and C

$$\left. \begin{aligned} \Delta_A U &= U(P_2, T_2, V_2, n_2) - U(P_1, T_1, V_1, n_1) \\ \Delta_C U &= U(P_1, T_1, V_1, n_1) - U(P_2, T_2, V_2, n_2) \end{aligned} \right\}$$

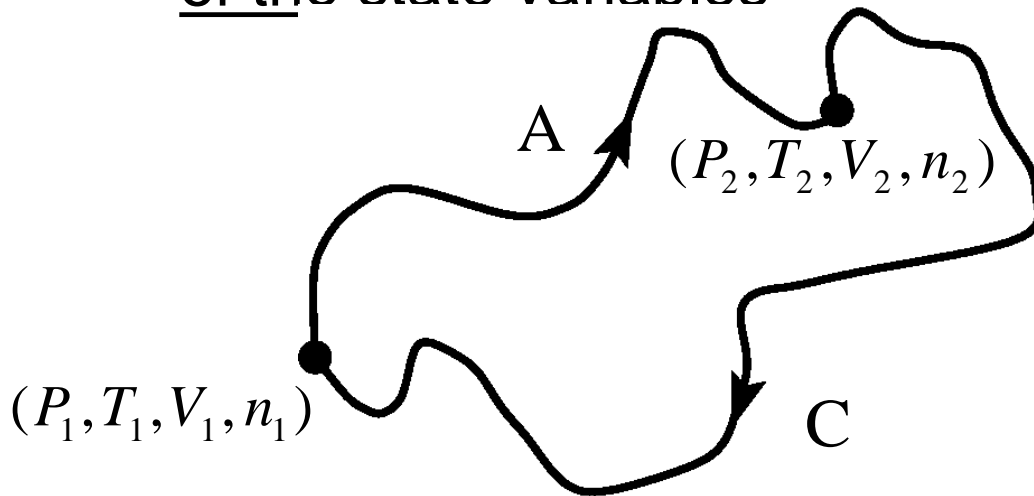
Thermodynamics: First law

- First law: **conservation of energy**

$$dU = dW + dQ$$

U is a unique function of the state variables

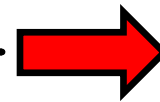
$$U = U(P, T, V, n)$$



Note the different directions for paths B and C

$$\Delta_A U = U(P_2, T_2, V_2, n_2) - U(P_1, T_1, V_1, n_1)$$

$$\Delta_C U = U(P_1, T_1, V_1, n_1) - U(P_2, T_2, V_2, n_2)$$



$$\Delta_A U + \Delta_C U = 0$$

$\Delta U = 0$ for any loop, whether reversible or irreversible

Thermodynamics is based on two laws

These are phenomenological laws

- First law: conservation of energy

$$dU = dW + dQ$$

$$\Delta U = W + Q$$

$$\oint dU = 0$$

U is a state function

- U : **internal energy** of the system
- Q : the **heat** in the process
- W : the **work** in the process

(Q and W are not state functions)

- Second law: for any spontaneous process

$$dS_{\text{tot}} = dS + dS_{\text{sur}} \geq 0$$

- S : **entropy** of the system

Summary (for a glossary see App. B of SG)

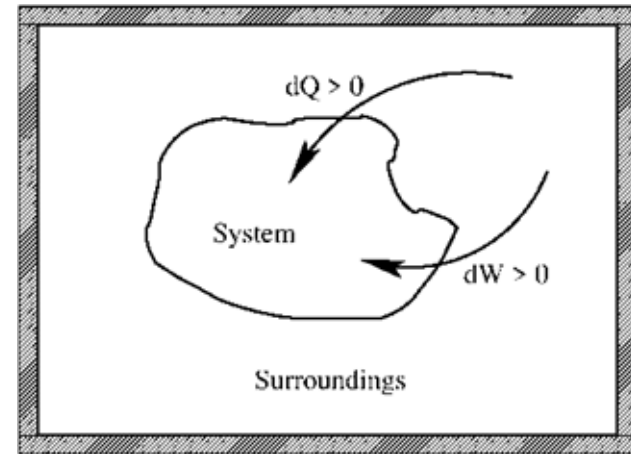
- First law: conservation of energy

$$dU = dW + dQ$$

$$\Delta U = \int dU = W + Q$$

$$\oint dU = 0$$

U is a state function



Reversible process

- Mechanical work

$$W = -\int P_{\text{ext}} dV \equiv -\int P dV$$

- Perfect gas

$$PV = nRT$$

Equation of state

- Perfect atomic gas

$$U = \frac{3}{2} nRT = \frac{3}{2} PV$$

Glossary

Microscopic On an atomic or molecular scale.

Macroscopic Seen from an helicopter view, in such a way that we can forget about microscopic processes (averaging).

System That part of the universe in which we are interested; we only consider macroscopic systems with many particles in thermodynamics.

Surroundings The rest of the universe we need to allow exchange of matter or energy with the system; is also a system, but not *the* system.

Thermal bath A heat reservoir (usually as surroundings), from which you can extract heat or to which you can deliver heat, without changing the temperature of the reservoir.

State variables Macroscopic quantities (P, V, T, n, \dots) that describe the thermodynamic state of a system. For a complete description a minimal amount of (independent) state variables is required.

Equation of state Relation between state variables that determines the possible states of the system in thermodynamic equilibrium.

Thermodynamic equilibrium A system is in thermodynamic equilibrium if the state variables of the system do not change spontaneously.

State function A (thermodynamic) single valued function of the (independent) state variables; The value of a state function is independent of the way the system has reached a certain state.

Reversible process A process during which the system is in thermodynamic equilibrium at every moment; with that a reversible process is also reversible.

Irreversible process A process that is not necessarily reversible.

Isothermal process A process that proceeds at constant temperature ($dT = 0$ for the system).

Isobaric process A process that proceeds at constant pressure ($dP = 0$ for the system).

Isochoric process A process that proceeds at constant volume ($dV = 0$ for the system).

Adiabatic process A process that proceeds without heat exchange with the environment ($dQ = 0$).

Isolated system No exchange between system and surroundings ($dW = dQ = dn = 0$).

Closed system No exchange of matter between system and surroundings ($dn = 0$); there can be exchange of work ($dW \neq 0$) or heat ($dQ \neq 0$).

Open system A non-closed system ($dn \neq 0$).

Homogeneous system A system in which every (macroscopic) subsystem has the same properties.

Isotropic system A system that has the same properties in all directions, such as an homogeneous fluid. A crystal is not isotropic.

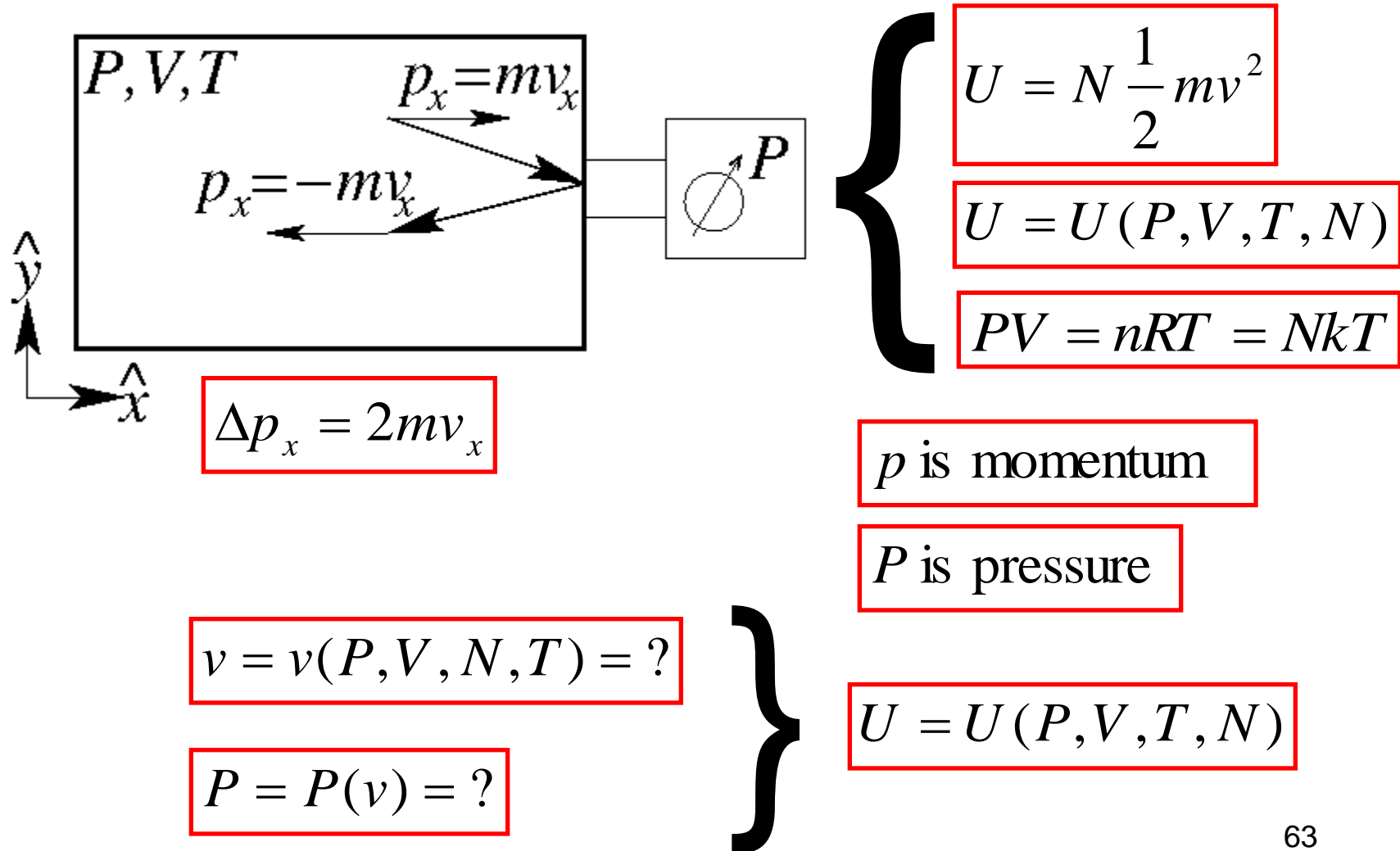
Intensive quantity Does not change if we enlarge the system; e.g. T and P .

Extensive quantity Doubles if we make the system twice as large; e.g. V and n .

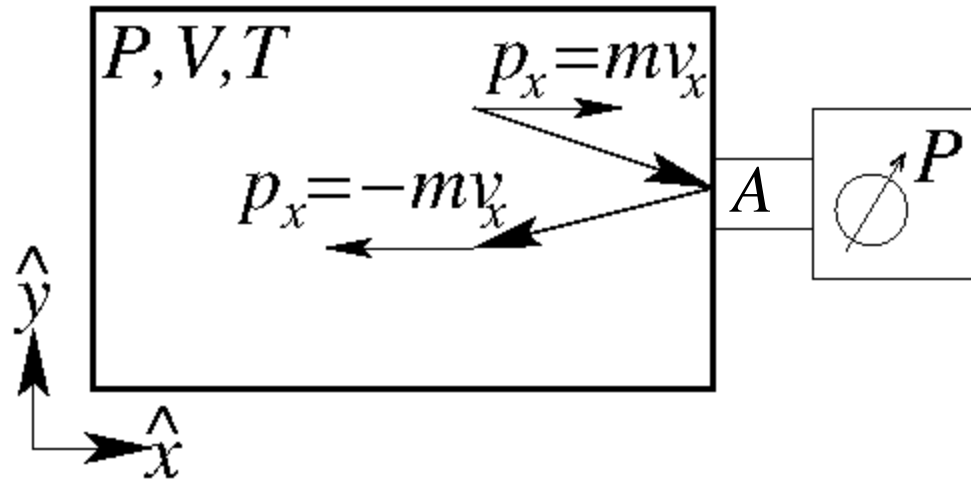
Statistical thermodynamics Relates microscopic processes and (macroscopic) thermodynamics.

Internal energy U of a perfect gas of N atoms

(Power point version of pages 4-5 of the Study)



Internal energy U of a perfect gas of N atoms



$$P = P(v) = ?$$

mean velocities

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$v_x = v_y = v_z$$

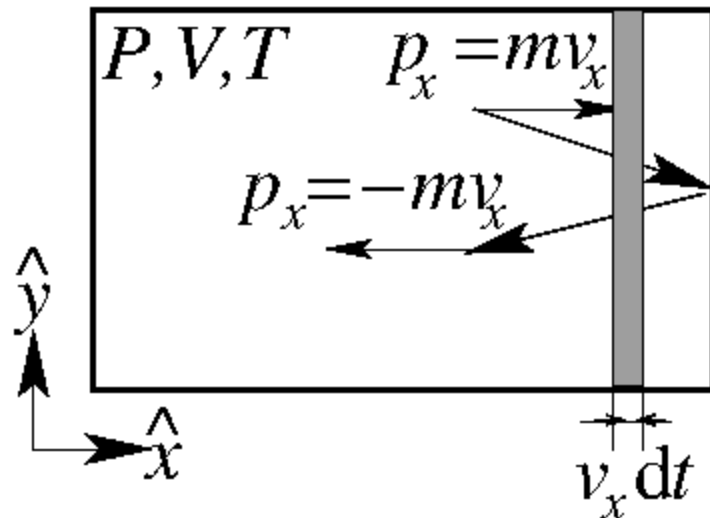


$$v_x^2 = v_y^2 = v_z^2 = \frac{1}{3} v^2$$

Newton

$$P = \frac{F_x}{A} = \frac{ma_x}{A} = \frac{m}{A} \frac{dv_x}{dt} = \frac{1}{A} \frac{dp_x}{dt}$$

Internal energy U of a perfect gas of N atoms



$$P = P(v) = ?$$

$$P = \frac{1}{A} \frac{dp_x}{dt}$$

ρ Number density (# atoms/V)

in dt

$$\frac{1}{2} \rho A v_x dt = \frac{1}{2} \frac{N}{V} A v_x dt$$

atoms have an impact

with

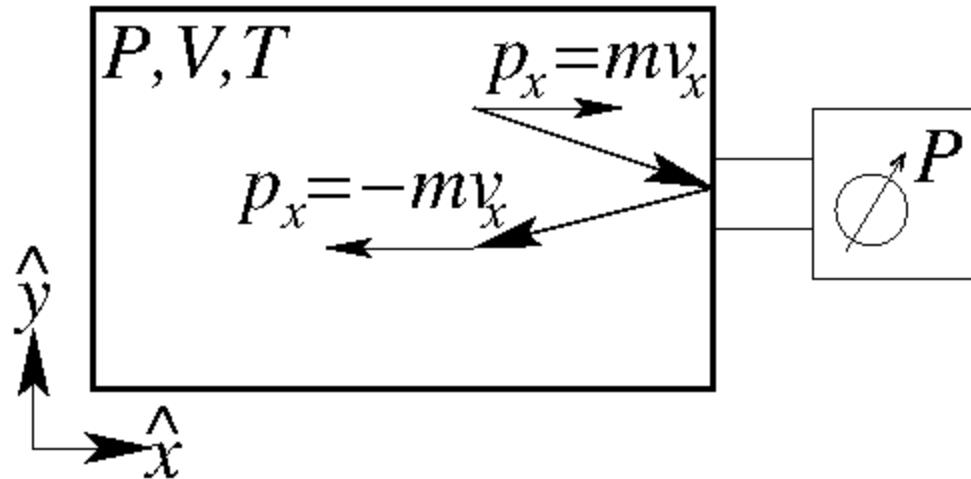
$$dp_x = \frac{1}{2} \frac{N}{V} A v_x dt \cdot 2mv_x = m \frac{N}{V} A v_x^2 dt$$

momentum transfer

so

$$\frac{dp_x}{dt} = m \frac{N}{V} A v_x^2$$

Internal energy U of a perfect gas of N atoms



$$P = P(v) = ?$$

momentum

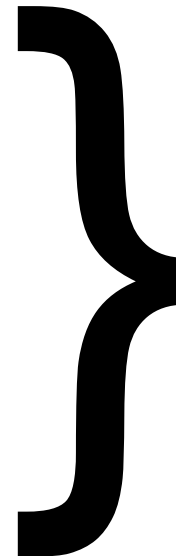
$$\frac{dp_x}{dt} = m \frac{N}{V} A v_x^2$$

pressure

$$P = \frac{1}{A} \frac{dp_x}{dt}$$

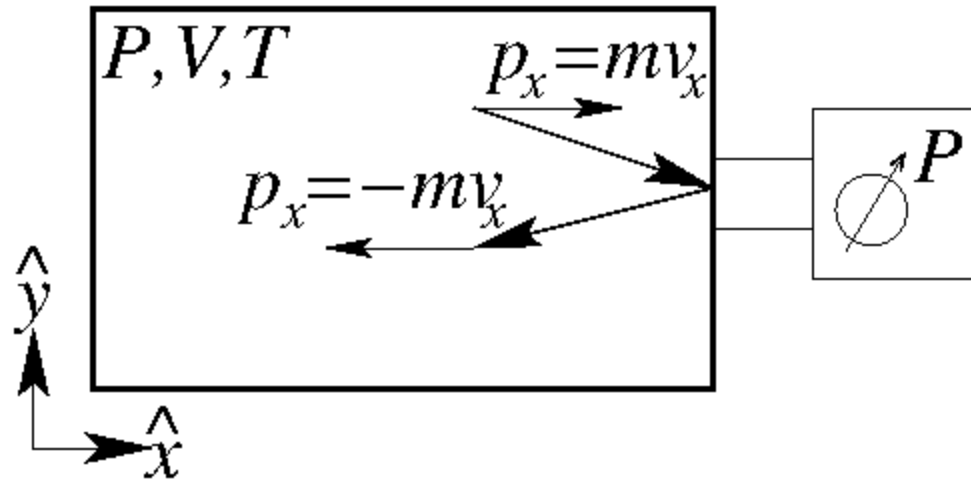
velocity

$$v_x^2 = \frac{1}{3} v^2$$



$$P = m \frac{N}{V} \frac{1}{3} v^2$$

Internal energy U of a perfect gas of N atoms



$$P = P(v) = ?$$

pressure

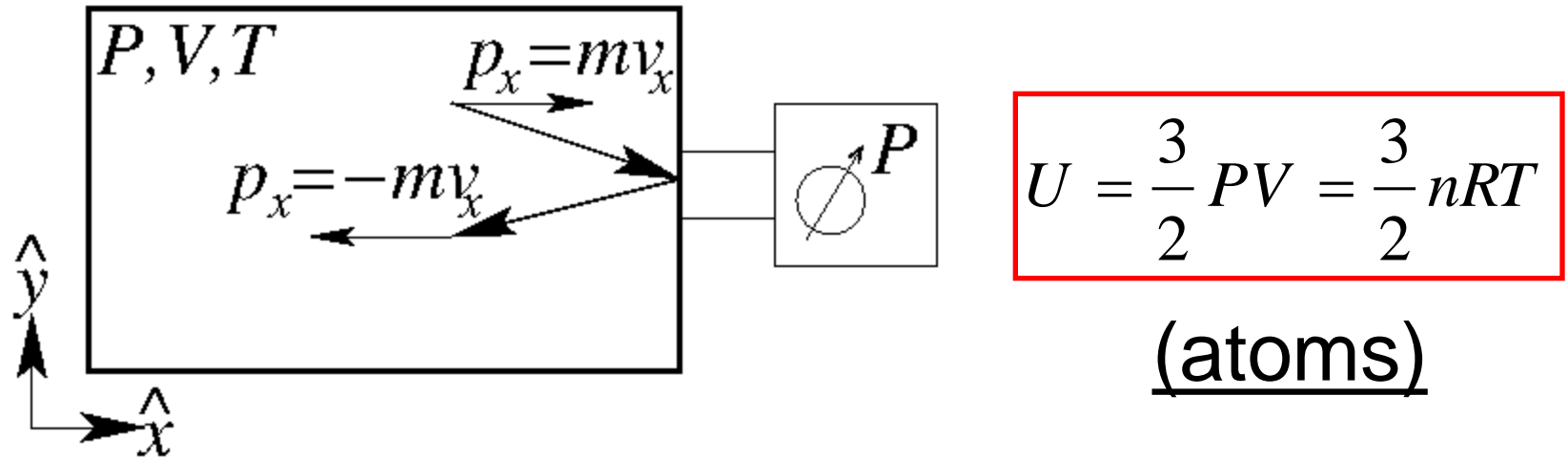
$$P = m \frac{N}{V} \frac{1}{3} v^2$$

internal energy

$$U = N \frac{1}{2} m v^2$$

$$U = \frac{3}{2} PV = \frac{3}{2} nRT$$

Internal energy U of a perfect gas **atoms**



for **molecules**

also rotational and vibrational contributions:

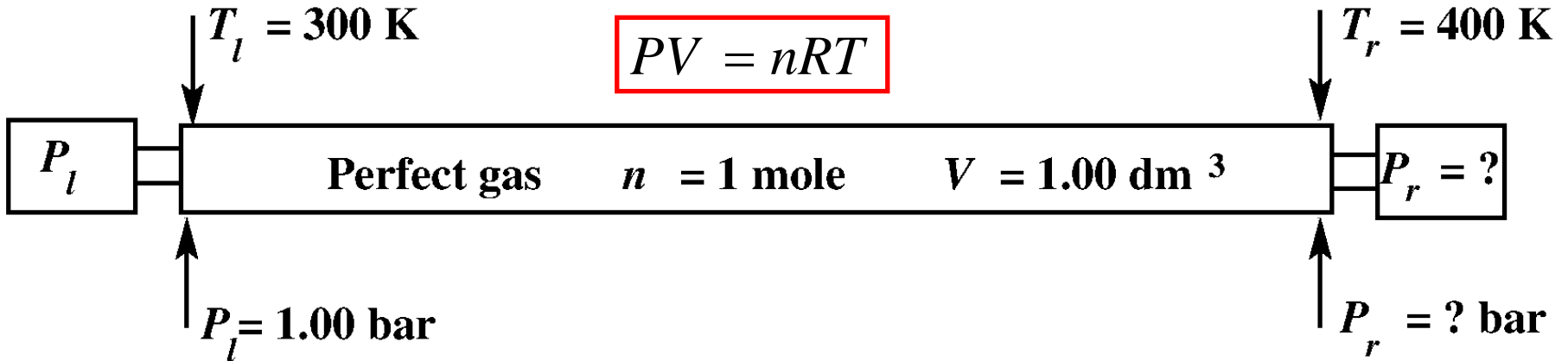
$$U = f PV = f nRT$$

$$f > \frac{3}{2}$$

Thermodynamics

Thermodynamics problem: My Auncle and I

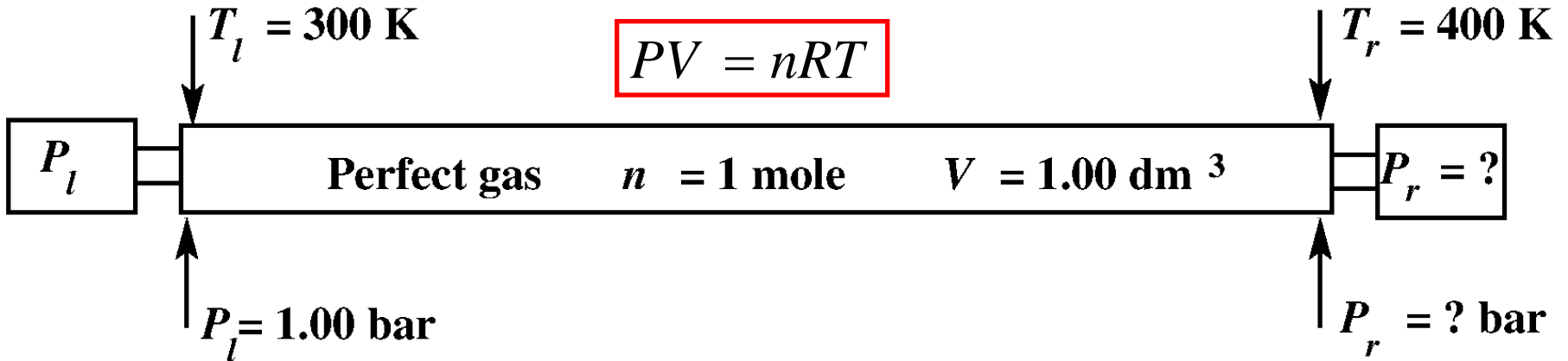
My auncle has a problem:



The problem is what will be the pressure on the right side P_r ?

Thermodynamics problem: My Auncle and I

My auncle has a problem:

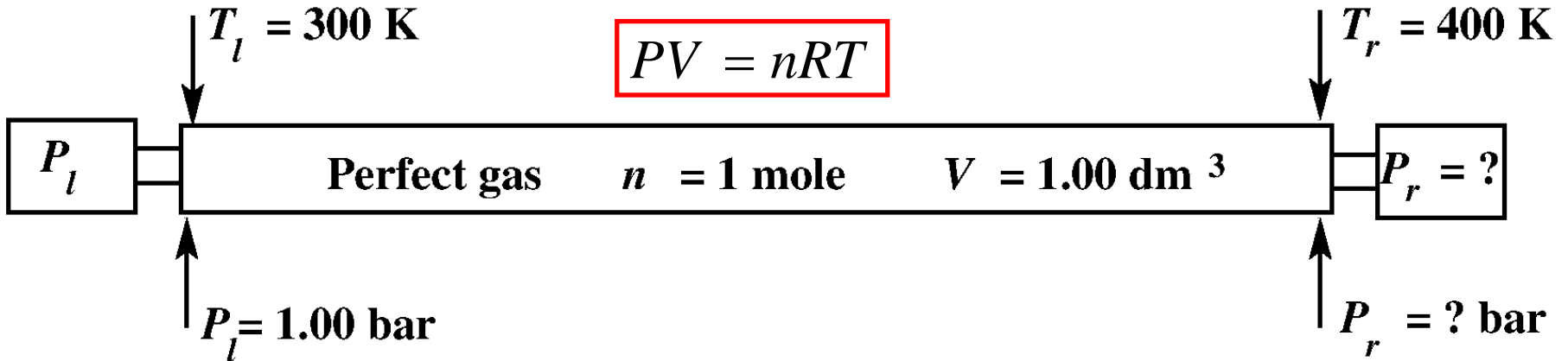


The problem is what will be the pressure on the right side P_r ?

- Possible answers:
- Possible answer 1: $P_r < P_l$
 - Possible answer 2: $P_r = P_l$
 - Possible answer 3: $P_r > P_l$

Thermodynamics problem: My Auncle and I

My auncle has a problem:



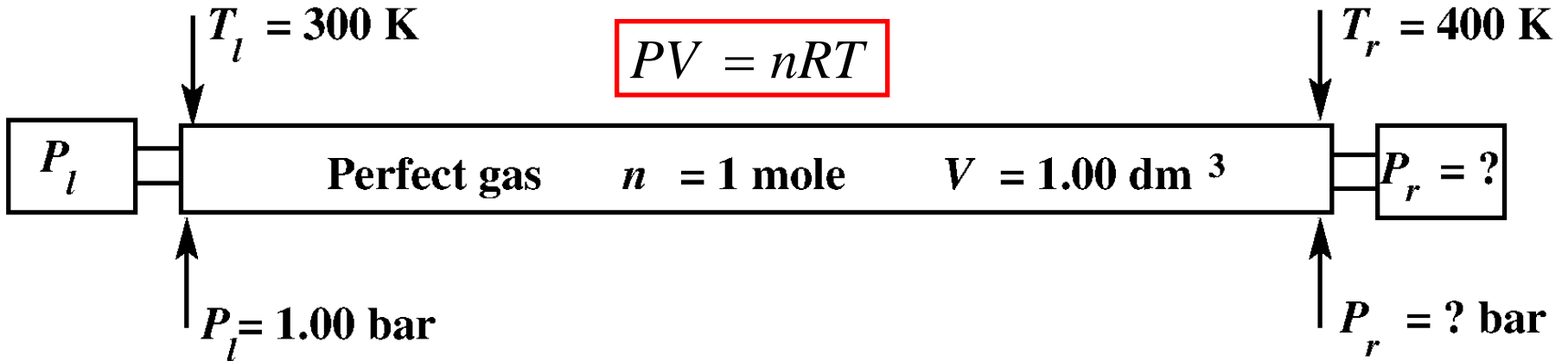
The problem is what will be the pressure on the right side P_r ?

My auncle says: the temperature is higher, but V is constant, so $P_r > P_l \rightarrow$ answer 3

- Possible answers:
- Possible answer 1: $P_r < P_l$
 - Possible answer 2: $P_r = P_l$
 - Possible answer 3: $P_r > P_l$

Thermodynamics problem: My Auncle and I

My auncle has a problem:



The problem is what will be the pressure on the right side P_r ?

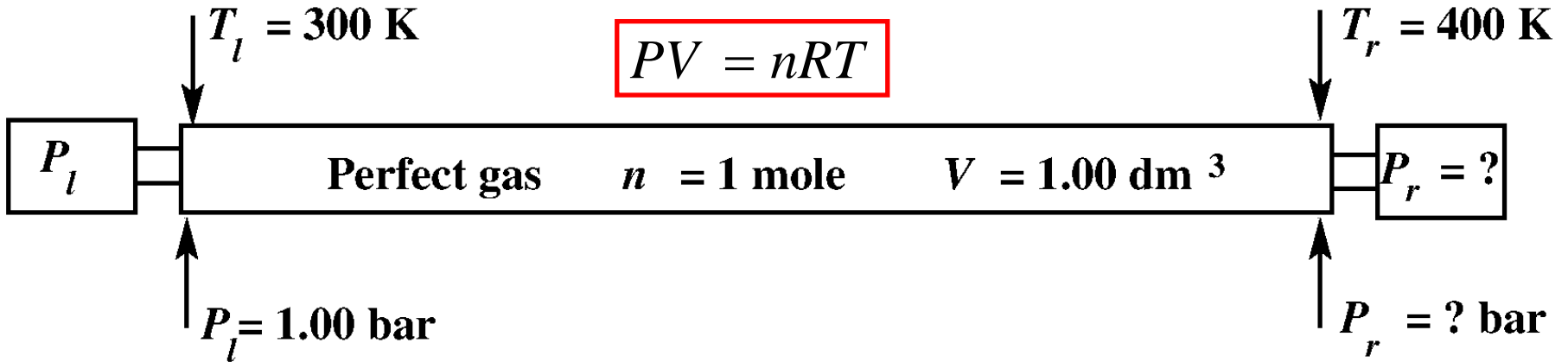
I (the student) say(s): yes, but for higher T the gas expands and will have locally a smaller density, so a much larger V , so $P_r < P_l \rightarrow 1$

Possible answers: {

- Possible answer 1: $P_r < P_l$
- Possible answer 2: $P_r = P_l$
- Possible answer 3: $P_r > P_l$

Thermodynamics problem: My Auntle and I

My auntle has a problem:



The problem is what will be the pressure on the right side P_r ?

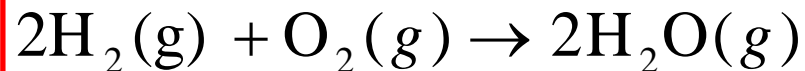
--My auntle says: the temperature is higher, but V is constant, so $P_r > P_l \rightarrow$ answer 3

--I (the student) say(s): yes, but for higher T the gas expands and will have locally a smaller density, so a much larger V , so $P_r < P_l \rightarrow$ 1

--Or does your reasoning give $P_r = P_l \rightarrow$ answer 2

Thermodynamics

Thermodynamics is about processes



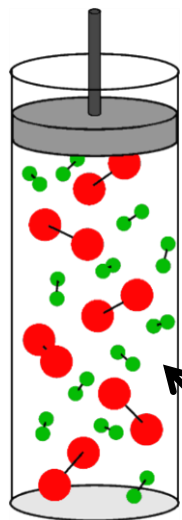
Some new definitions:

- Partial pressure P_i in a mixture of perfect or non-perfect gases:

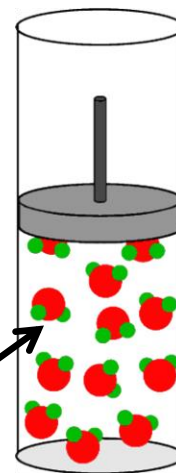
$$P_i \equiv x_i P$$

- Mole fraction x_i of component i :

$$x_i = \frac{n_i}{n} = \frac{n_i}{\sum_j n_j}$$



Initial state



Final state

$$x_{\text{H}_2} = \frac{n_{\text{H}_2}}{n} = \frac{n_{\text{H}_2}}{n_{\text{H}_2} + n_{\text{O}_2}} = \frac{2}{3}$$

$$x_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}}} = 1$$