

Study Guide Thermodynamics 2, 2023/2024

Hugo Meekes
Solid State Chemistry
HG03.625; 53200
Hugo.Meekes@science.ru.nl



Literature

- Book: Physical Chemistry; P.W. Atkins.; edition 12, 11, 10 or 9, Oxford University Press
- Study guide: This study guide.
- All information will be available via the link in Brightspace or directly at <http://www.vsc.science.ru.nl/hugom/Thermo2/Thermo2.html>



Aim

- Primary: Insight and skills
- Secondary: Knowledge



Organisation

• Introduction

Thermodynamics is built on two phenomenological perceptions, the first law and the second law describing the conditions for spontaneous processes. In the course Thermodynamics these laws were treated together with a few basic applications. In the course Thermodynamics 2 this basic perception is deepened and applied to more complex systems.

The following subjects will be treated:

- Stability of phases and phase diagrams - Phase transitions - Surface tension - Thermodynamics of mixtures - Thermodynamics of solutions - Activity - Electrolytes - The Boltzmann equation



• Literature

- Physical Chemistry; P.W. Atkins.; edition 12, 11, 10 or 9, Oxford University Press
- Study guide: will be made available online during the course of the lectures and provides additional information to the book



• Lectures, are on-campus and not recorded (earlier recordings are available).

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.

A survey of subjects in Atkins which have been treated in the first year course Thermodynamics (2021/2022) can be found in Appendix E; See <https://dullenslab.com/teaching/> for the course of 2022/2023.



The present course Thermodynamics 2 will start with a concise recapitulation of the essential notions treated in Thermodynamics and will overall treat the following parts of the literature (SG is Study Guide, * refers to add. info ternary phase diagrams on the home page)

| Date | Atkins ed. 12 or 11 | SG | ed. 10 | ed. 9 | Thermo 2: subjects |
|-------|---------------------|-----------|---------|---------------|------------------------------|
| 06/09 | 2D+3E | 3-8,14-15 | 2D+3D | 2.10-11+3.7-8 | Exact diff., Molec. gasses |
| 13/09 | 4 | 9-11 | 4 | 4 | Phase diagr. of pure subst. |
| 20/09 | 5A | 9-13 | 5A | 5.1-5 | P, x -phase diagrams |
| 27/09 | 5B-C | - | 5B-C | 5.5-8 | T, x -phase diagrams |
| 04/10 | 5D-E | - | 5C-D | 5.9+* | $s-l$, ternary phase diagr. |
| 11/10 | 14C.2-4 | 16 | 16C.2-4 | 17.8-10+6 | Interfaces, Chem. Eq. |
| 18/10 | 6+5F | 17-18 | 6+5F | 6+5.13 | Electrochem., Stat. Th. |



- **Tutorials are on-campus and not recorded.**

The tutorial exercises will be available before, and the solutions after, each tutorial on the website: <http://www.vsc.science.ru.nl/hugom/Thermo2/Thermo2.html>.

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 exercises in the exam. There are three groups, for the Science, Chemistry and Premaster students, respectively. Students from other studies can choose freely which group to join.



| Group | cohort | room | day | time | TA |
|-------|-----------|---------------------|----------|-------------|------------------------------------|
| 1 | Chemistry | HG00.514 | Thursday | 10:30-12:15 | Tobias Dijkhuis & Jannes Peters |
| 2 | Premaster | Transitorium 00.005 | Thursday | 10:30-12:15 | Hugo Meekes |
| 3 | Science | HG00.622 | Thursday | 13:30-15:15 | t.b.a. |



- **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 (with answers) will appear online at the end of the course.

Two lists of formulae (without further comments) will be provided at the exam. The first list is the same as was provided in the course Thermodynamics (Appendix C) and the second list adds the new formulae (Appendix D).



Graphical calculators are NOT allowed during the exam (regular ones are).

Formulae first year course Thermodynamics

$$PV = nRT = NkT$$

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

$$\Delta U = W + Q$$

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

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

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

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

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

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

$$H = U + PV$$

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

$$A = U - TS$$

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

$$G = H - TS$$

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

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

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

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

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

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

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

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

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

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

$$S = k \ln W$$

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

Formulae Thermodynamics 2

$$\left(\frac{\partial V}{\partial T} \right)_{P,W',n_i} = - \left(\frac{\partial S}{\partial P} \right)_{T,W',n_i}$$

$$X_i = \left(\frac{\partial X}{\partial n_i} \right)_{P,T,n_{j \neq i}}$$

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

$$P_j = x_j P_j^*$$

$$P_j = y_j P$$

$$P_B = x_B K_B$$

$$\left(\frac{\partial \mu_\beta}{\partial P} \right)_T - \left(\frac{\partial \mu_\alpha}{\partial P} \right)_T = \Delta_{trs} V$$

$$\left(\frac{\partial \mu_\beta}{\partial T} \right)_P - \left(\frac{\partial \mu_\alpha}{\partial T} \right)_P = -\Delta_{trs} S$$

$$P = P^* \exp \left(\frac{V_m \Delta P}{RT} \right)$$

$$\frac{dP}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V} = \frac{\Delta_{trs} H}{T \Delta_{trs} V}$$

$$\frac{d \ln P}{dT} \approx \frac{\Delta_{trs} H}{RT^2}$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{trs} H} \right) x_B \quad \ln x_B = \frac{\Delta_{fus} H}{R} \left[\frac{1}{T_{fus}} - \frac{1}{T} \right]$$

$$\mu = \mu^\ominus + RT \ln a = \mu^\ominus + RT \ln x + RT \ln \gamma$$

$$\mu = \mu^\ominus + RT \ln a = \mu^\ominus + RT \ln \frac{b}{b^\ominus} + RT \ln \gamma$$

$$F = C - P + 2$$

$$n_\alpha l_\alpha = n_\beta l_\beta$$

$$\Delta_{solv} G^\ominus = -\frac{z_i^2 e^2 N_A}{8\pi \epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r} \right)$$

$$\gamma_\pm = (\gamma_+^p \gamma_-^q)^{\frac{1}{p+q}}$$

$$\log \gamma_\pm = -|z_+ z_-| A \sqrt{I}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^\ominus}$$

$$A = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^\ominus}{2\epsilon^3 R^3 T^3} \right)^{\frac{1}{2}}$$

$$P_{in} = P_{out} + \frac{2\gamma}{r} \quad P = \rho gh \quad w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \quad \gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \Theta_c$$



Subjects treated in the first year course Thermodynamics.

In the course Thermodynamics (2022) parts from Part 1 (Equilibrium) of Atkins have been treated. In addition a few subjects treated can be found in the Study Guide to Thermodynamics (<http://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html>).

For the course of 2023 see <https://dullenslab.com/teaching/>.



| Week | Sections (edition 11 Atkins) | Subject |
|------|----------------------------------|--|
| 1 | 1A + 1C + 2A + 2B (+ 2E) + SG4-8 | Gases, First Law of Thermodynamics, Reversible processes |
| 2 | 3A + 3B + 3D1 + 3E2a-c + SG9-13 | Entropy, Second Law of Thermodynamics Free energy, Irreversible processes |
| 3 | SG14-18 + 5A1b-c + 5B + 5F1-2 | Chemical Potential, Activity Mixtures, Colligative properties |
| 4 | 2C + 3D2a + 6A + 6B | Thermochemistry, Chemical Equilibria T, P -dependence equilibria |
| 5 | 6C1-3 + 6D(p.224) | Electrochemistry, Standard Potential, Nernst-equation |
| 6 | 3A3 + SG19-22 | Second Law of Thermodynamics, Efficiency |
| 7 | 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



| Week | Sections (edition 10 Atkins) | Subject |
|------|----------------------------------|--|
| 1 | 1A + 1C + 2A + 2B (+ 2E) + SG4-8 | Gases, First Law of Thermodynamics, Reversible processes |
| 2 | 3A + 3C1 + 3D2a-c + SG9-13 | Entropy, Second Law of Thermodynamics Free energy, Irreversible processes |
| 3 | SG14-18 + 5A1b-c + 5B + 5E1-2 | Chemical Potential, Activity Mixtures, Colligative properties |
| 4 | 2C + 3C2a + 6A + 6B | Thermochemistry, Chemical Equilibria T, P -dependence equilibria |
| 5 | 6C1-3 + 6D(p.267) | Electrochemistry, Standard Potential, Nernst-equation |
| 6 | 3A3 + SG19-22 | Second Law of Thermodynamics, Efficiency |
| 7 | 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



| Week | Sections (edition 9 Atkins) | Subject |
|------|---------------------------------|--|
| 1 | 1.1 - 1.4 + 2.1 - 2.6 + SG4-8 | Gases, First Law of Thermodynamics, Reversible processes |
| 2 | 3.1 - 3.3a + 3.5 + 3.9 + SG9-13 | Entropy, Second Law of Thermodynamics Free energy, Irreversible processes |
| 3 | SG14-18 + 5.1b-c + 5.5 - 5.6 | Chemical Potential, Activity Mixtures, Colligative properties |
| 4 | 2.7 - 2.9 + 3.6 + 6.1 - 6.4 | Thermochemistry, Chemical Equilibria T, P -dependence equilibria |
| 5 | 6.5 - 6.8 | Electrochemistry, Standard Potential, Nernst-equation |
| 6 | 3.2 + SG19-22 | Second Law of Thermodynamics, Efficiency |
| 7 | 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

Glossary

Microscopic On an atomic or molecular scale.

Macroscopic Seen from a 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. 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.

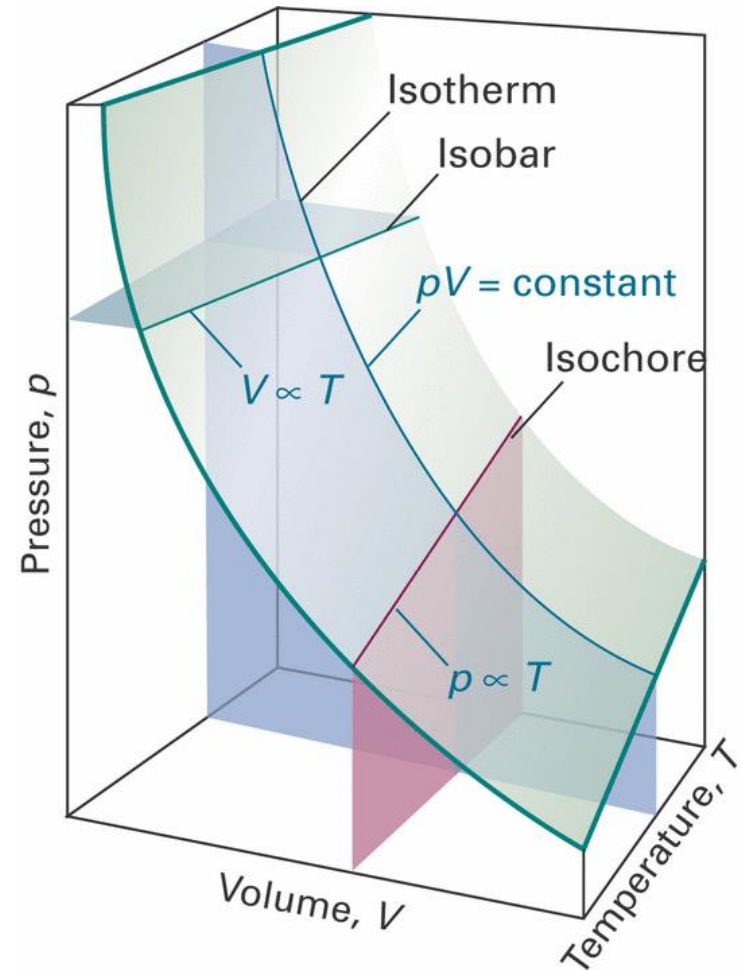
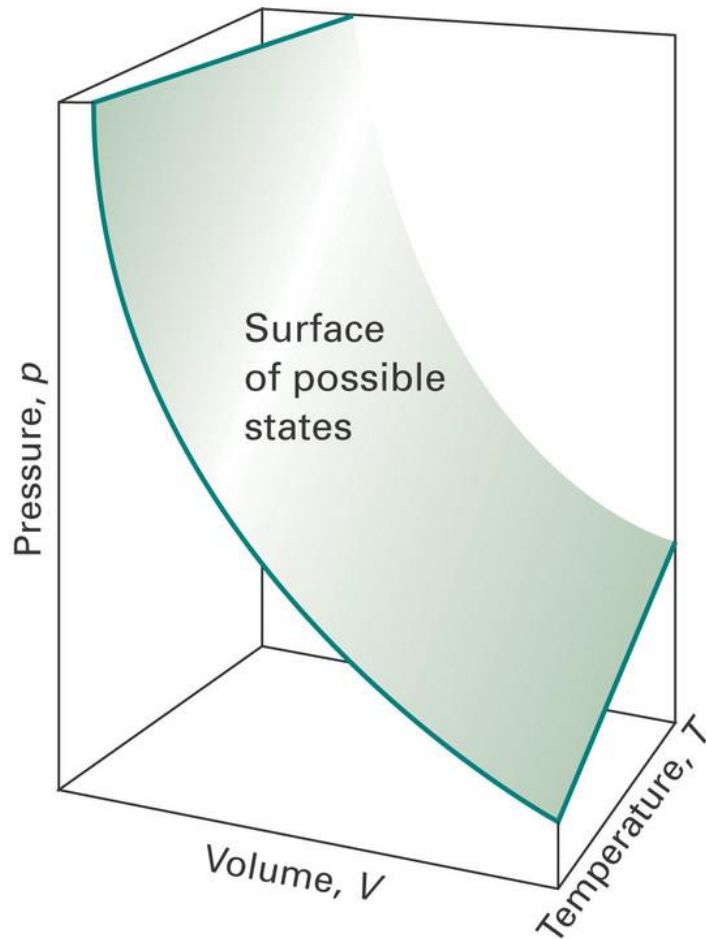
Isotropic system A system that has the same properties in all directions, such as a homogeneous fluid. A crystal is not isotropic.

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.

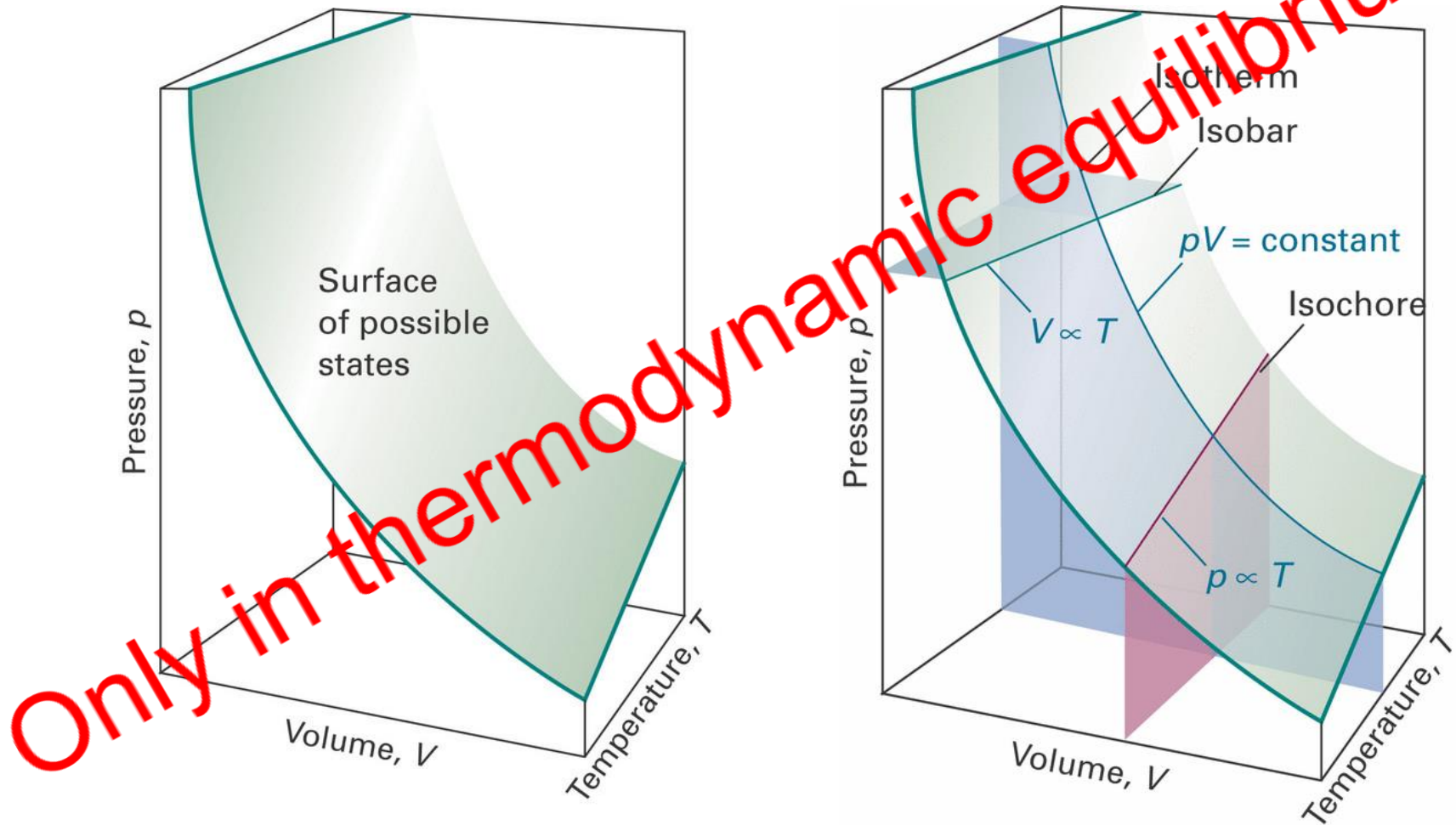
Perfect gas: $PV = nRT = NkT$ (equation of state)



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

(\Rightarrow 4 variables reduced to 3)

Perfect gas: $PV = nRT = NkT$ (equation of state)



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

(=> 4 variables reduced to 3)



$$nR = Nk = nN_A k$$

$\frac{\text{J/mol K}}$ $\frac{\text{J/K}}$

↓ ↓

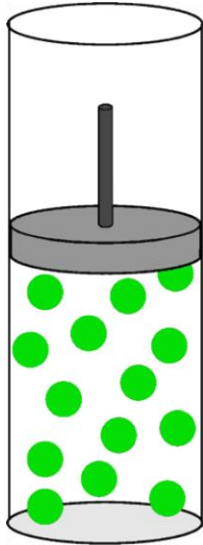
↓ ↓

$$R = N_A k$$

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

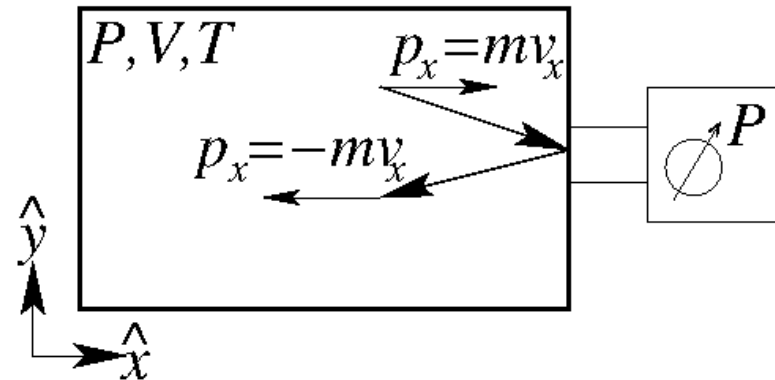
Amadeo Avogadro di Quaregna e Cerreto

Perfect gas: from atoms to molecules



Atomic perfect gas

$$PV = nRT$$



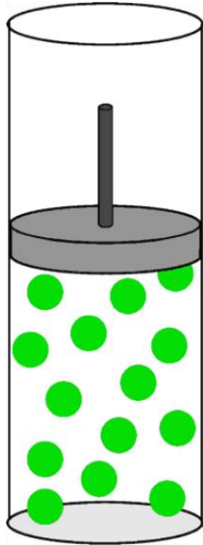
(Study guide p.3-4)



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

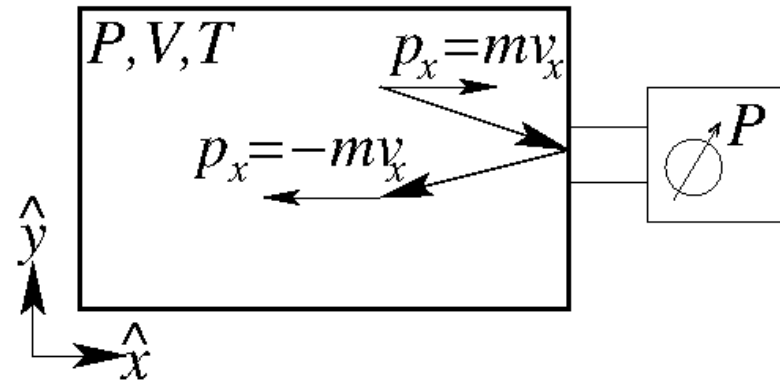
Internal energy
of the system

Perfect gas: from atoms to molecules



Atomic perfect gas

$$PV = nRT$$



(Study guide p.3-4)



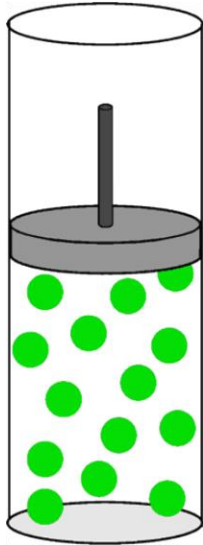
$$U = \frac{3}{2} PV = \frac{3}{2} nRT$$

Internal energy
of the system

Only for atomic perfect gas!

Perfect gas: from atoms to molecules

(Study guide p.17-18)

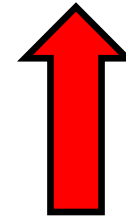


Atomic perfect gas

$$PV = nRT$$

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

Internal energy



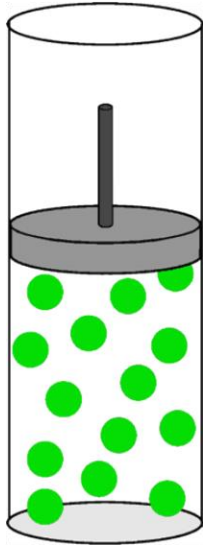
$$U = 3N \frac{1}{2} kT$$

Internal energy of a **system**
with **3N** degrees of freedom

(equipartition theorem)

Perfect gas: from atoms to molecules

(Study guide p.17-18)



Atomic perfect gas

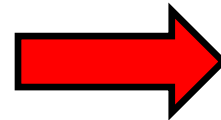
$$PV = nRT$$

$$U = \frac{1}{2} kT$$

Internal energy

per degree of freedom
(equipartition theorem)

$$U = 3N \frac{1}{2} kT$$



$$Nk = nR$$

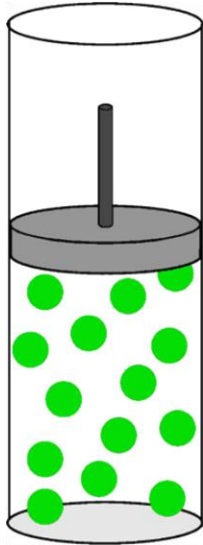
$$U = \frac{3}{2} nRT$$

(x, y, z) $(N \text{ atoms})$

$3N$ degrees of freedom

Perfect gas: from atoms to molecules

Only Translational
degrees of freedom

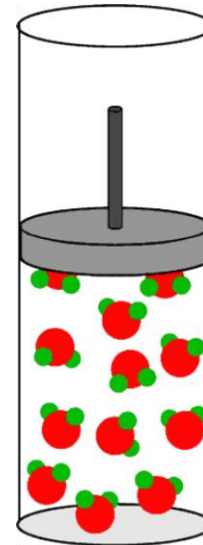


Atomic perfect gas

$$U = 3N \frac{1}{2} kT = U^T$$

$$N_T = 3$$

Also Rotational and Vibrational
degrees of freedom



Molecular perfect gas

$$N_R = ?$$

$$N_V = ?$$

Perfect gas: from atoms to molecules

Rotational

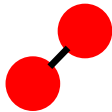
degrees of freedom

atom



$$N_R = 0$$

linear

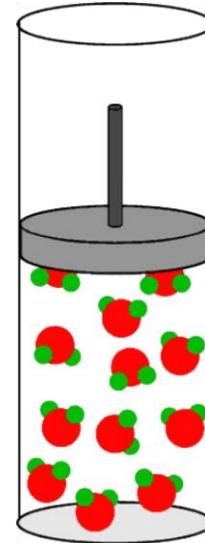


$$N_R = 2$$

non-linear



$$N_R = 3$$



Molecular perfect gas

$$U^R = MN_R \frac{1}{2} kT$$

(M molecules) ($N_R = \#$ Rotation axes)

Perfect gas: from atoms to molecules

Rotational

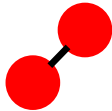
degrees of freedom

atom



$$N_R = 0$$

linear



$$N_R = 2$$

non-linear



$$N_R = 3$$

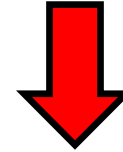
$$U^R = MN_R \frac{1}{2} kT$$

Vibrational

degrees of freedom

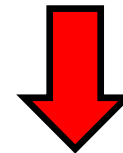
In total: N atoms in

M molecules

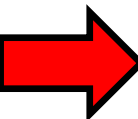


$3N$ degrees of freedom

$$3N = N_T M + N_R M + N_V M$$



$$3N = 3M + N_R M + N_V M$$



Perfect gas: from atoms to molecules

Rotational

degrees of freedom

Vibrational

degrees of freedom

atom

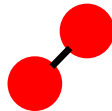


$$N_R = 0$$



$$N_V = 0$$

linear



$$N_R = 2$$



$$N_V = 3N_m - 5$$

non-linear



$$N_R = 3$$



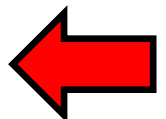
$$N_V = 3N_m - 6$$

$$U^R = MN_R \frac{1}{2} kT$$

$$N_m \equiv \frac{N}{M}$$

$$N_V = 3 \frac{N}{M} - 3 - N_R$$

N_m : # atoms/molecule



Perfect gas: from atoms to molecules

Rotational

degrees of freedom

Vibrational

degrees of freedom

atom

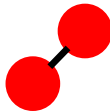


$$N_R = 0$$



$$N_V = 0$$

linear



$$N_R = 2$$



$$N_V = 3N_m - 5$$

non-linear



$$N_R = 3$$



$$N_V = 3N_m - 6$$

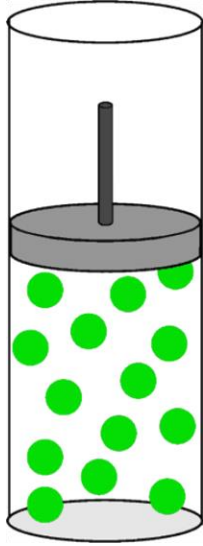
Vibrational energy

$$U^V = 2MN_V \frac{1}{2} kT$$



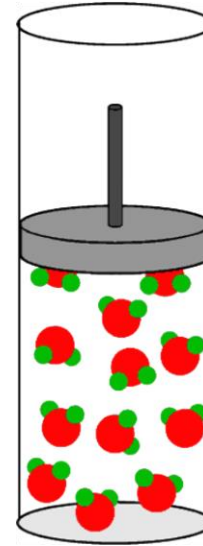
Chemical bond: kinetic and potential energy

Perfect gas: from atoms to molecules



(Study guide p.17-18)

Perfect gas
 $PV = nRT$
 obeys the
 equipartition theorem
 (**high T and low P**)



Atomic perfect gas

$$U = U^T = \frac{3}{2} NkT$$

Exercise 1

$$U = (3 + N_R + 2N_V) \frac{1}{2} MkT$$

$$Nk = nR$$

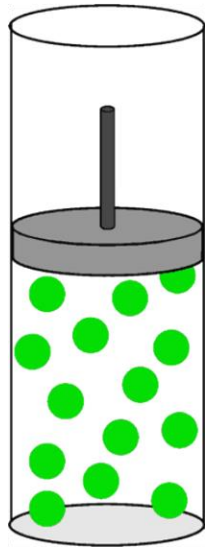
$$Mk = nR$$

$$C_V = \frac{3}{2} nR$$

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V$$

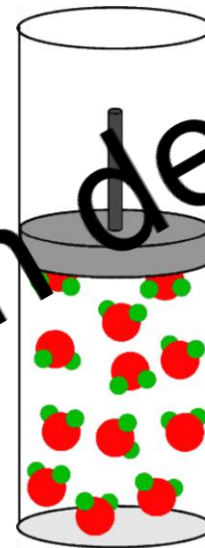
$$C_V = (3 + N_R + 2N_V) \frac{1}{2} nR$$

Perfect gas: from atoms to molecules



(Study guide p.17-18)

Perfect gas
 $PV = nRT$
obeys the equipartition theorem
(high T and low P)



Atomic perfect gas

Molecular perfect gas

$$U = U^T = \frac{3}{2} NkT$$

Exercise 1

$$U = (3 + N_R + 2N_V) \frac{1}{2} MkT$$

$$Nk = nR$$

$$Mk = nR$$

$$C_V = \frac{3}{2} nR$$

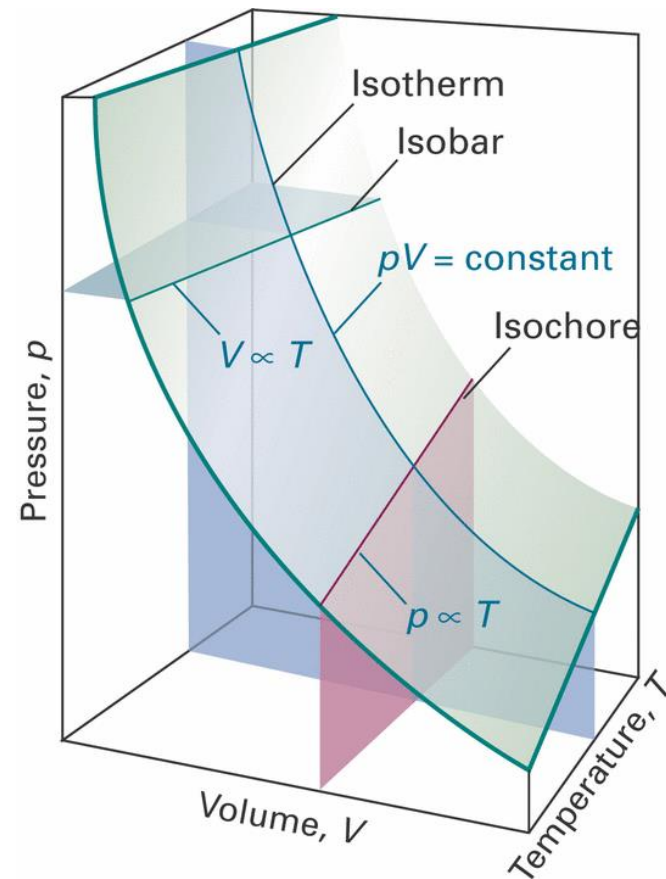
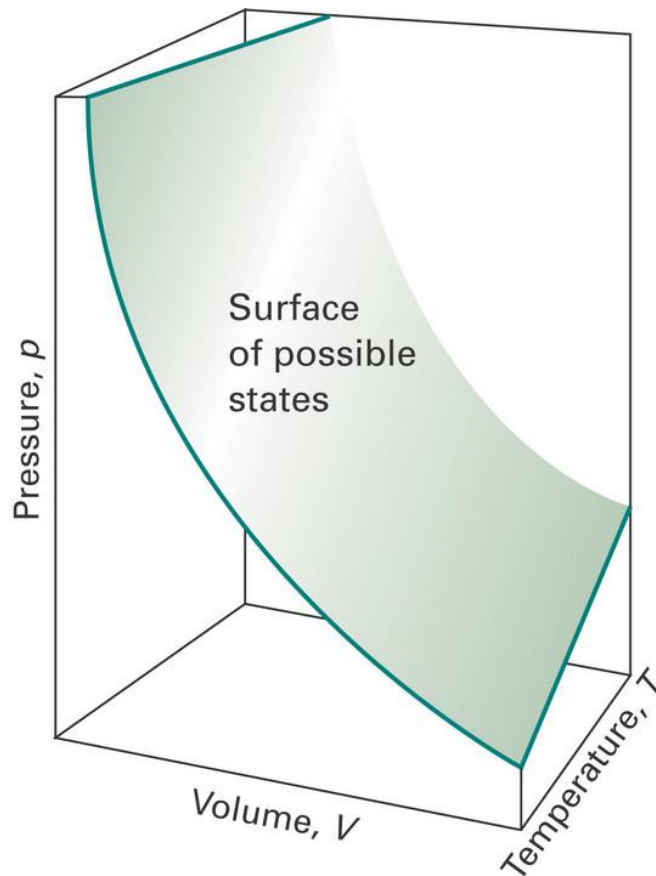
$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_V = (3 + N_R + 2N_V) \frac{1}{2} nR$$

Let's work this out in detail

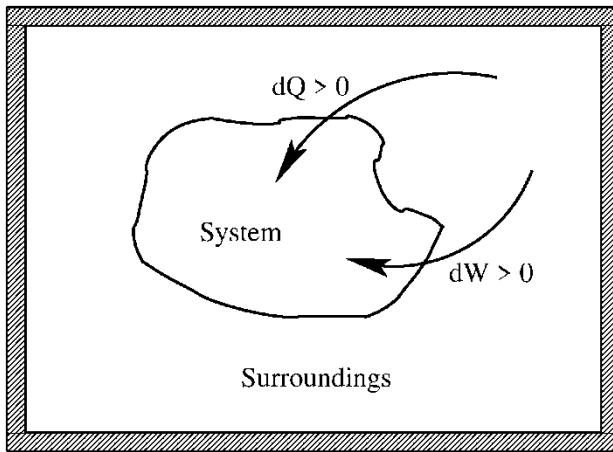
Perfect gas: $PV = nRT = NkT$ (equation of state)

Only for the system in equilibrium



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

General case: equilibrium thermodynamics



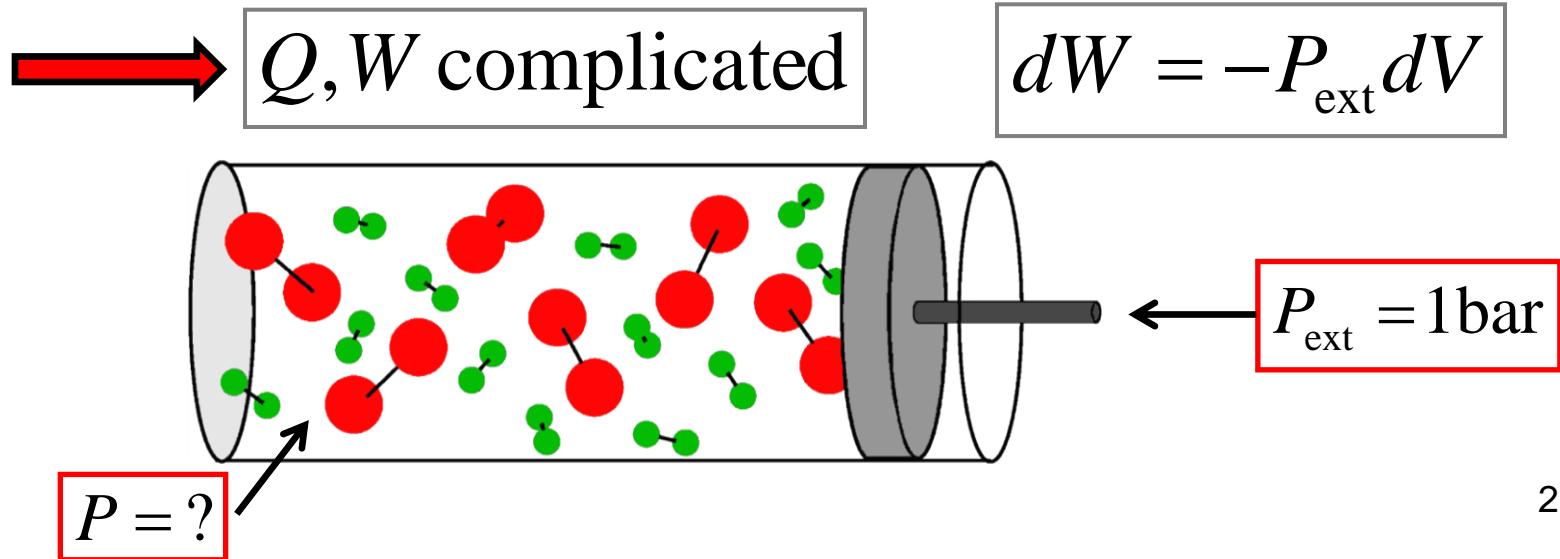
process

$$Q = \text{heat}$$

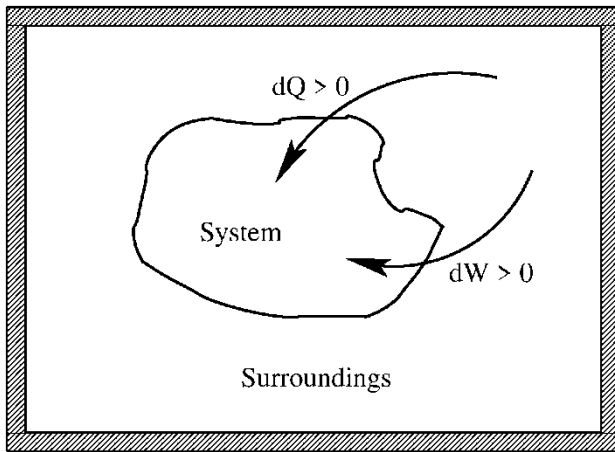
$$W = \text{work}$$

(Study guide p.5-10)

Irreversible processes: non-equilibrium and spontaneous



General case: equilibrium thermodynamics



process

$$Q = \text{heat}$$

$$W = \text{work}$$

(Study guide p.5-10)

Irreversible processes: non-equilibrium and spontaneous



Q, W complicated

$$dW = -P_{\text{ext}} dV$$

Reversible processes: always equilibrium and not spontaneous



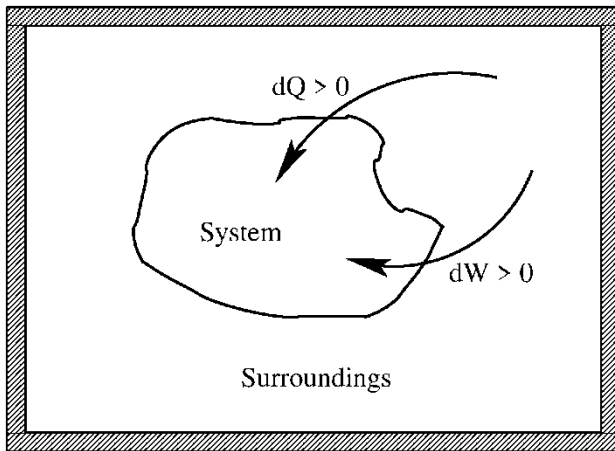
$$dW^{\text{rev}} = -PdV$$

$$dQ^{\text{rev}} = TdS$$

entropy

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

General case: equilibrium thermodynamics



First law:

$$dU = dQ + dW$$

$$dU^{\text{irr}} = dU^{\text{rev}}$$



$$dQ + dW = TdS - PdV$$

$$dU = dQ + dW = TdS - PdV$$

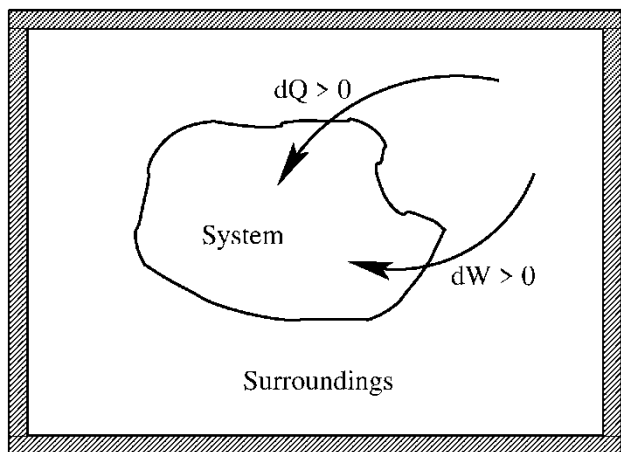
irreversible

reversible

First law: dU for an irreversible process can be determined by an alternative reversible process

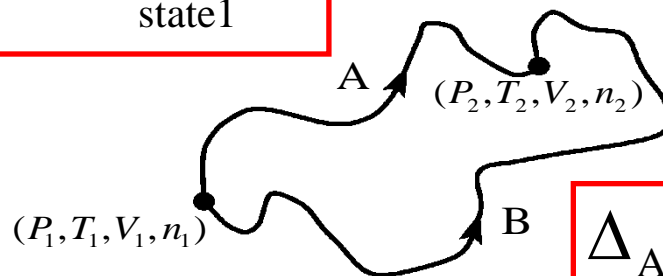
entropy $dS \equiv \frac{dQ^{\text{rev}}}{T}$

General case: equilibrium thermodynamics



$$\Delta U = \int_{\text{state 1}}^{\text{state 2}} dU$$

U is a state function



$$dU = dQ + dW = TdS - PdV$$

irreversible

reversible

First law: dU for an irreversible process can be determined by an alternative reversible process

entropy $dS \equiv \frac{dQ^{\text{rev}}}{T}$

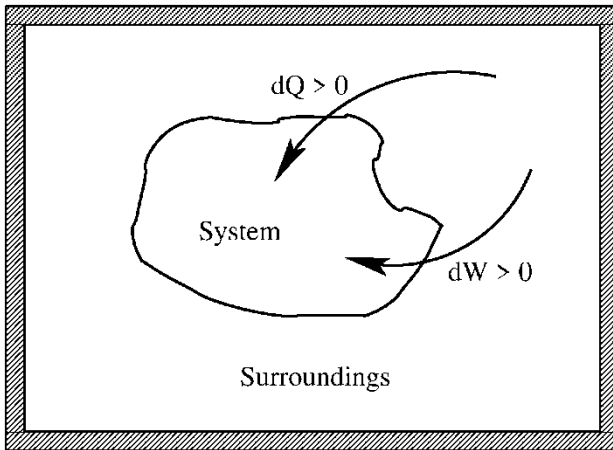
General case: equation of state

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

Only for the system in equilibrium



only three independent variables



$$P, V, T, n$$

are the state variables
of the system

For a closed system: n constant ($dn = 0$)



only two independent variables

Total differential of a state function: U


$$dU = TdS - PdV$$

characteristic equation

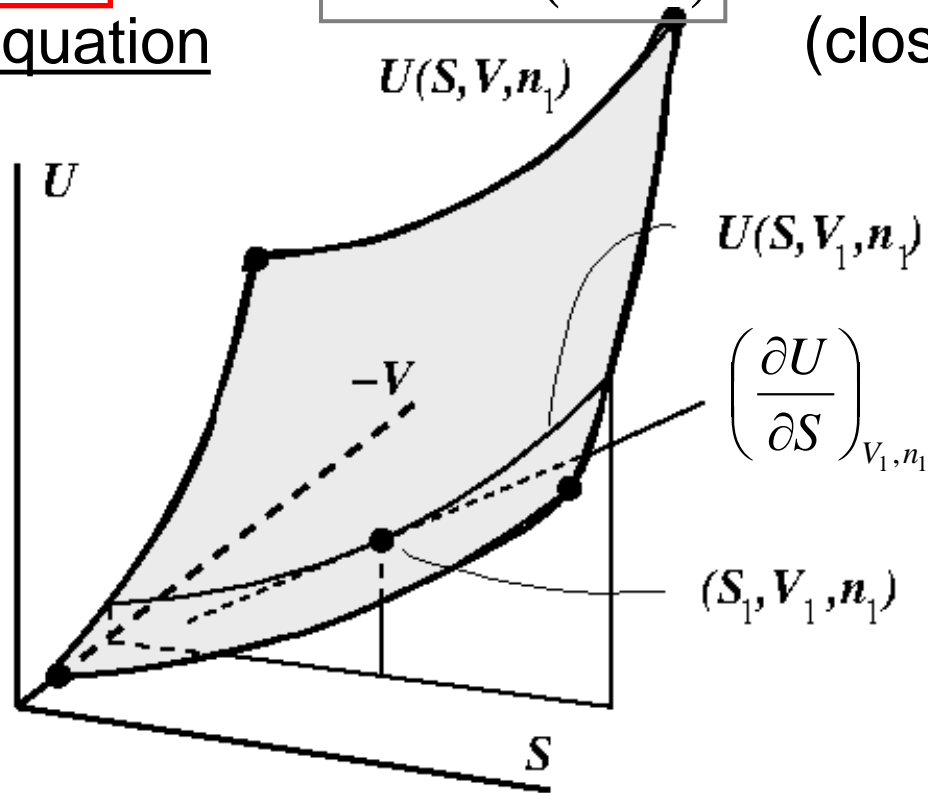
$$U = U(S, V)$$

$$dn = 0$$

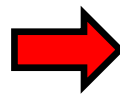
(closed system)

First law:

$$dU = dQ + dW$$



$$dU|_{V, n} = \left(\frac{\partial U}{\partial S}\right)_{V, n} dS$$



$$\Delta U|_{V, n} = \int \left(\frac{\partial U}{\partial S}\right)_{V, n} dS$$

Total differential of a state function: U

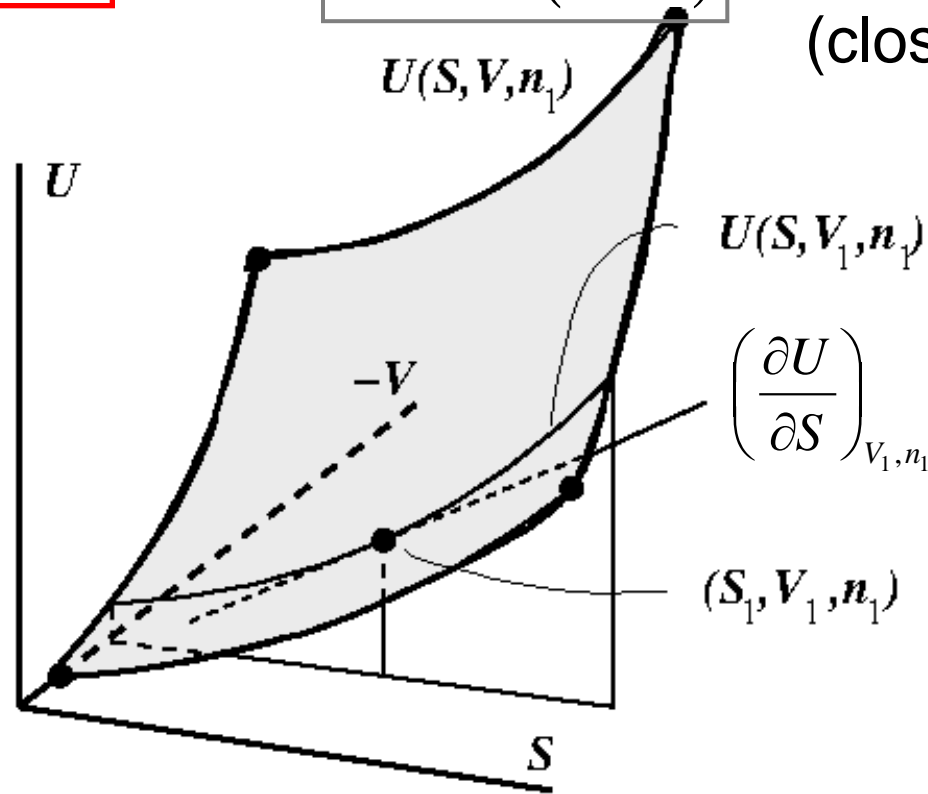
$$dU = TdS - PdV$$



$$U = U(S, V)$$

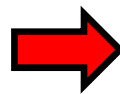
$$dn = 0$$

(closed system)



$$\left(\frac{\partial U}{\partial S}\right)_{V, n} \equiv T$$

$$dU|_{V, n} = \left(\frac{\partial U}{\partial S}\right)_{V, n} dS$$



$$\Delta U|_{V, n} = \int \left(\frac{\partial U}{\partial S}\right)_{V, n} dS$$

Total differential of a state function: U

$$dU = TdS - PdV$$

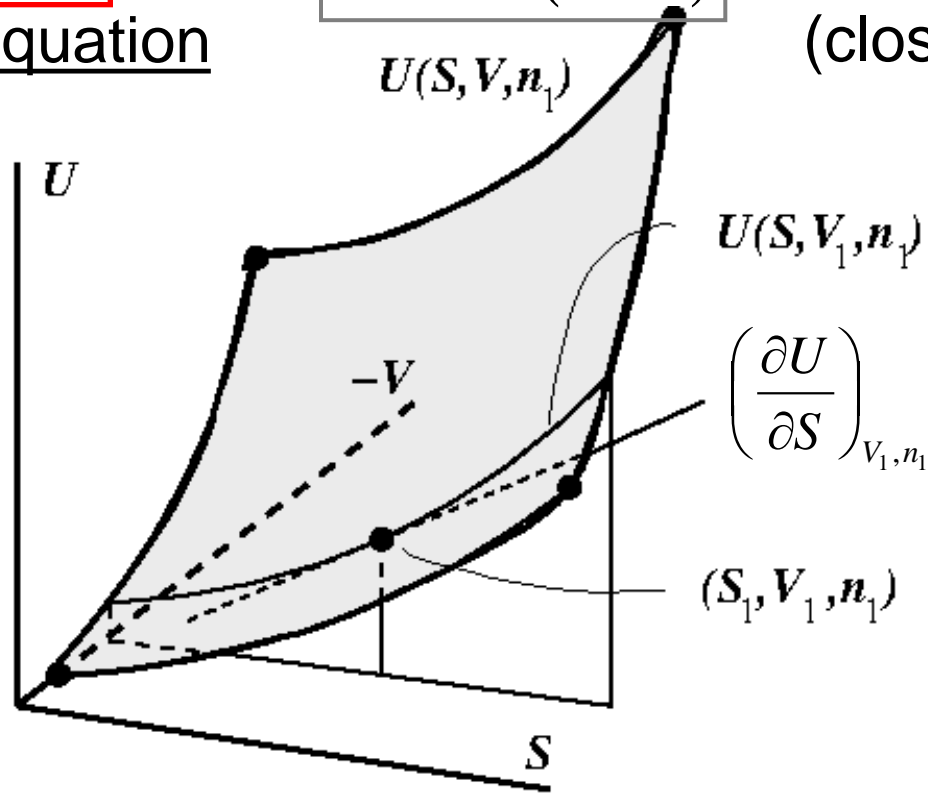
characteristic equation



$$U = U(S, V)$$

$$dn = 0$$

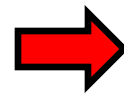
(closed system)



$$\left(\frac{\partial U}{\partial S}\right)_{V, n} \equiv T$$



$$dU|_{V, n} = \left(\frac{\partial U}{\partial S}\right)_{V, n} dS = TdS$$



$$\Delta U|_{V, n} = \int TdS$$

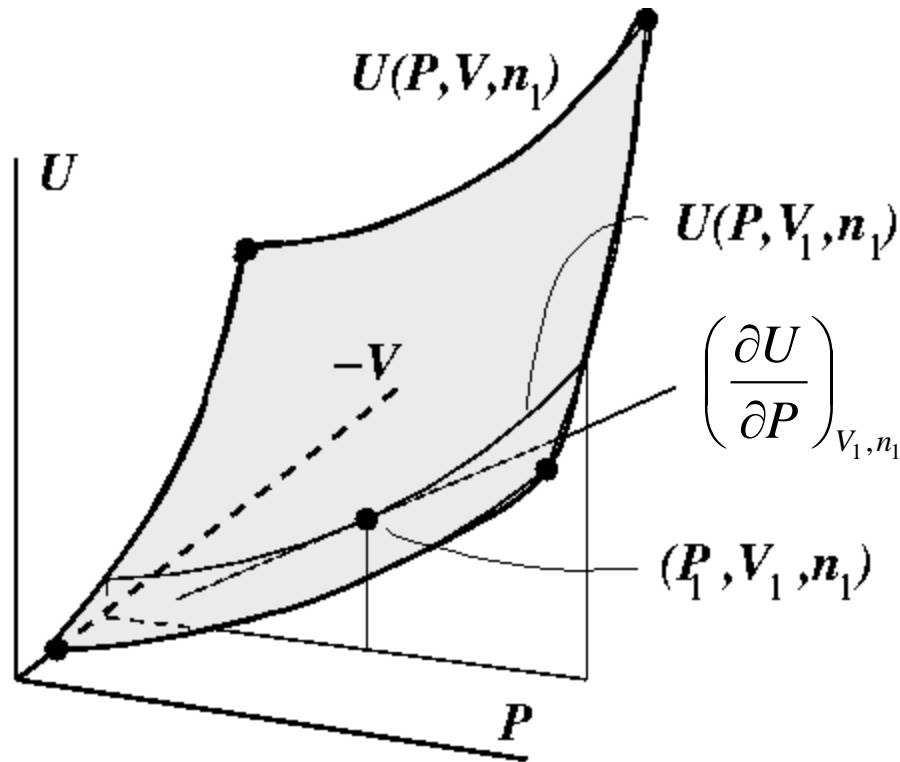
Total differential of a state function: U

(SG: appendix A)

$$dn = 0$$

(closed system)

Choose
 P and V
as
independent
variables



T
follows
from the
equation
of state

$$dU|_{V,n} = \left(\frac{\partial U}{\partial P} \right)_{V,n} dP$$

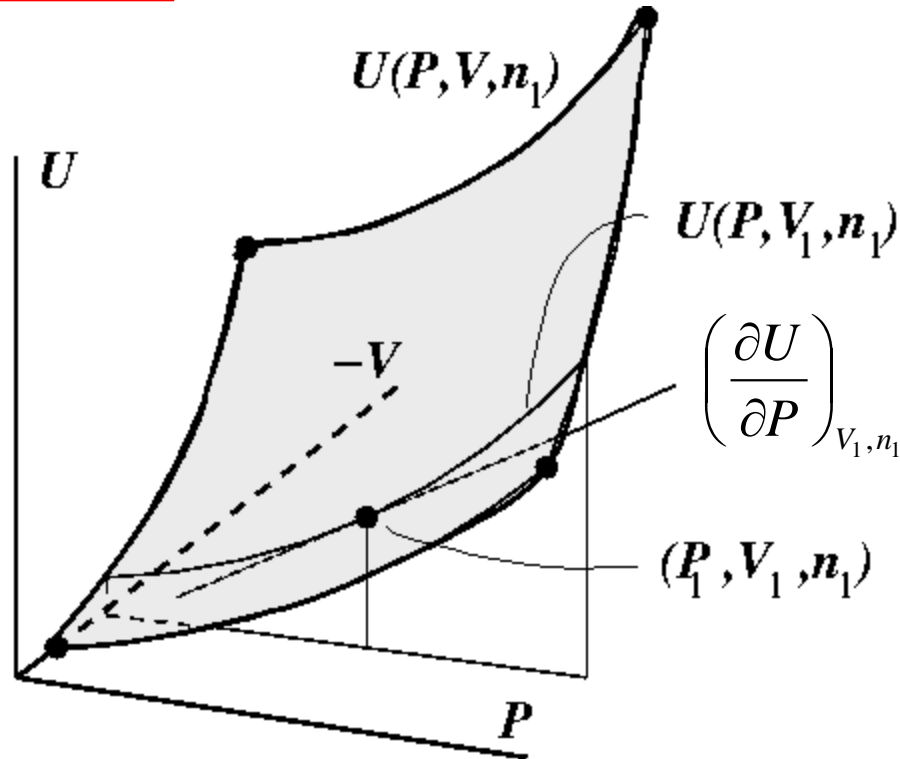
$$\Delta U|_{V,n} = \int \left(\frac{\partial U}{\partial P} \right)_{V,n} dP$$

Total differential of a state function: U

$$dU = TdS - PdV \quad (\text{characteristic equation})$$

$$dn = 0$$

(closed system)



T
follows
from the
equation
of state

dP is not the most convenient variable for dU

$$dU|_{V,n} = \left(\frac{\partial U}{\partial P} \right)_{V,n} dP$$

$$\Delta U|_{V,n} = \int \left(\frac{\partial U}{\partial P} \right)_{V,n} dP$$

Introduce new energy function: Enthalpy H

(SG: page 6)

Enthalpy H

$$H \equiv U + PV$$

$$dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

Consequence: heat capacity differs for U and H

$$dU \equiv dQ + dW \equiv dQ - PdV$$

(equilibrium)

$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$dH \equiv TdS + VdP = dQ + VdP$$

$$C_P \equiv \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P$$

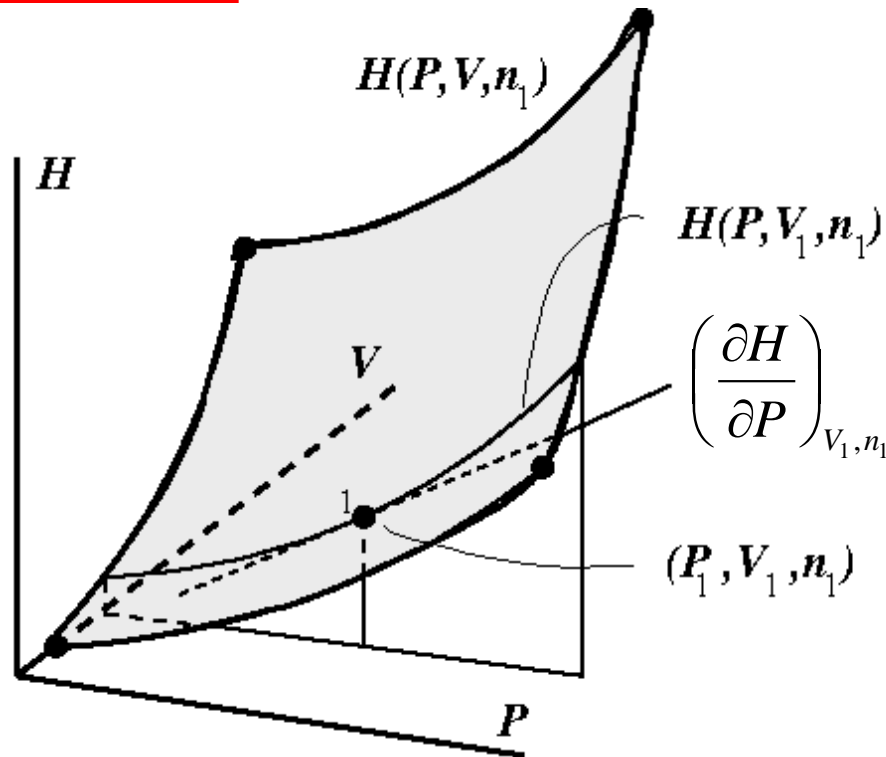
Introduce new energy function: Enthalpy H

$$dH = TdS + VdP$$

$$dn = 0$$

(closed system)

Choose
 P and V
as
independent
variables



T
follows
from the
equation
of state

$$dH|_{V,n} = \left(\frac{\partial H}{\partial P} \right)_{V,n} dP$$

$$\Delta H|_{V,n} = \int \left(\frac{\partial H}{\partial P} \right)_{V,n} dP$$

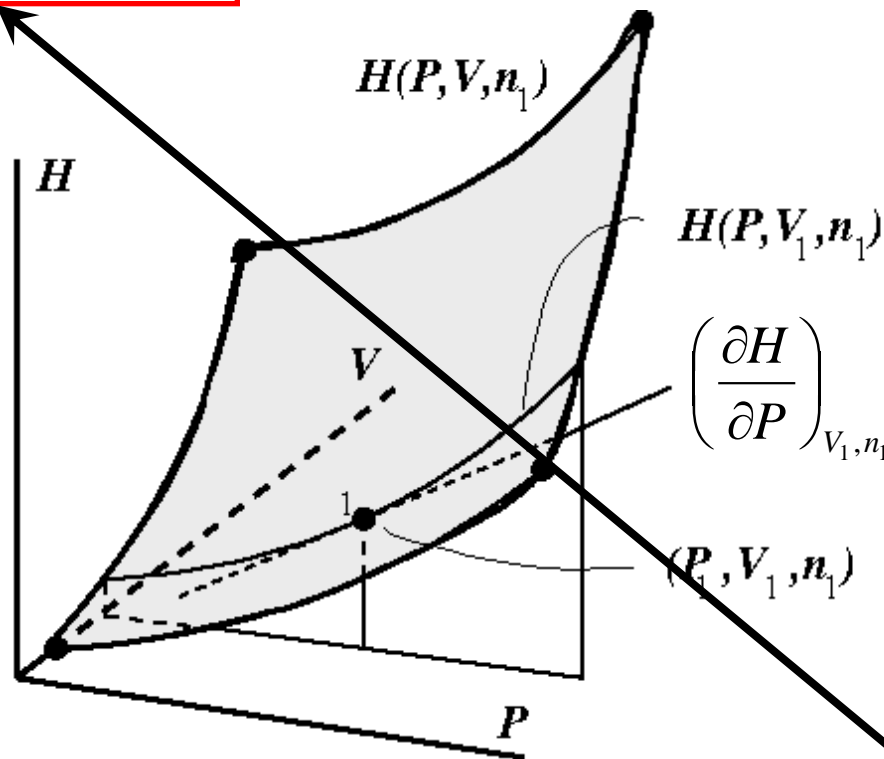
Introduce new energy function: Enthalpy H

$$dH = TdS + VdP$$

$$dn = 0$$

(closed system)

T
follows
from the
equation
of state



Constant V has less use in characteristic eq.

$$dH|_{V,n} = \left(\frac{\partial H}{\partial P} \right)_{V,n} dP$$

$$\Delta H|_{V,n} = \int \left(\frac{\partial H}{\partial P} \right)_{V,n} dP$$

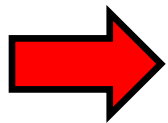
Helmholtz free energy and Gibbs free energy

(SG: page 8-10)

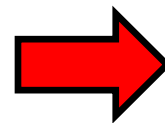
Helmholtz free energy A

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT = TdS - PdV - TdS - SdT$$



$$dA = -PdV - SdT$$



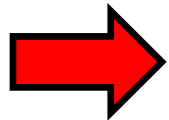
$$W_{\text{delivered}}^{\text{max}} = \Delta A|_T$$

Gibbs free energy G defined via the enthalpy H

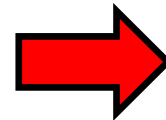
$$G \equiv H - TS$$

$$H \equiv U + PV$$

$$dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$$



$$dG = VdP - SdT$$



$$W_{\text{delivered}}^{\text{max}} = \Delta G|_{P,T}$$

Total differential of a state function:
Choose appropriate energy function

For a choice S and V : $dU = TdS - PdV$

For a choice S and P : $dH = TdS + VdP$

For a choice V and T : $dA = -PdV - SdT$

For a choice P and T : $dG = VdP - SdT$

Characteristic
equations

Total differential of a state function:
Choose appropriate energy function

For a choice S and V : $dU = TdS - PdV$

For a choice S and P : $dH = TdS + VdP$

For a choice V and T : $dA = -PdV - SdT$

For a choice P and T : $dG = VdP - SdT$

Characteristic equations

Choice of P and V is possible but very inconvenient
[PV] = J and [ST] = J, so choose S, V or S, P or V, T or P, T

Choice of eg. T and P for H is tedious but possible
and can be advantageous

Exercise 4

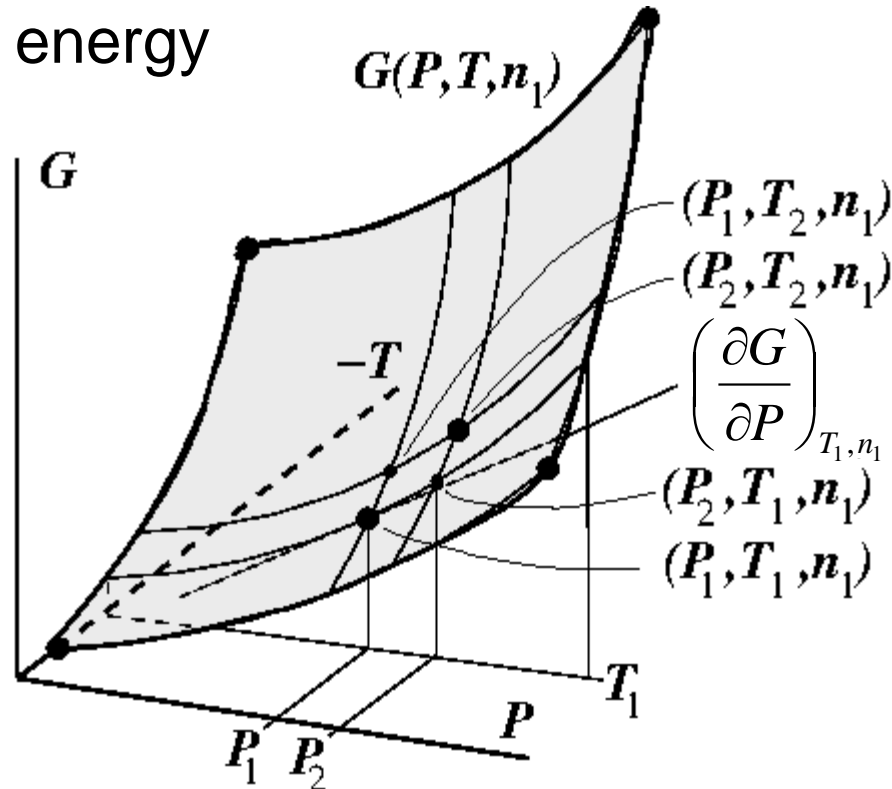
Total differential of a state function: G

$$dG = VdP - SdT$$

Gibbs free energy

$$dn = 0$$

(closed system)



V
follows
from the
equation
of state

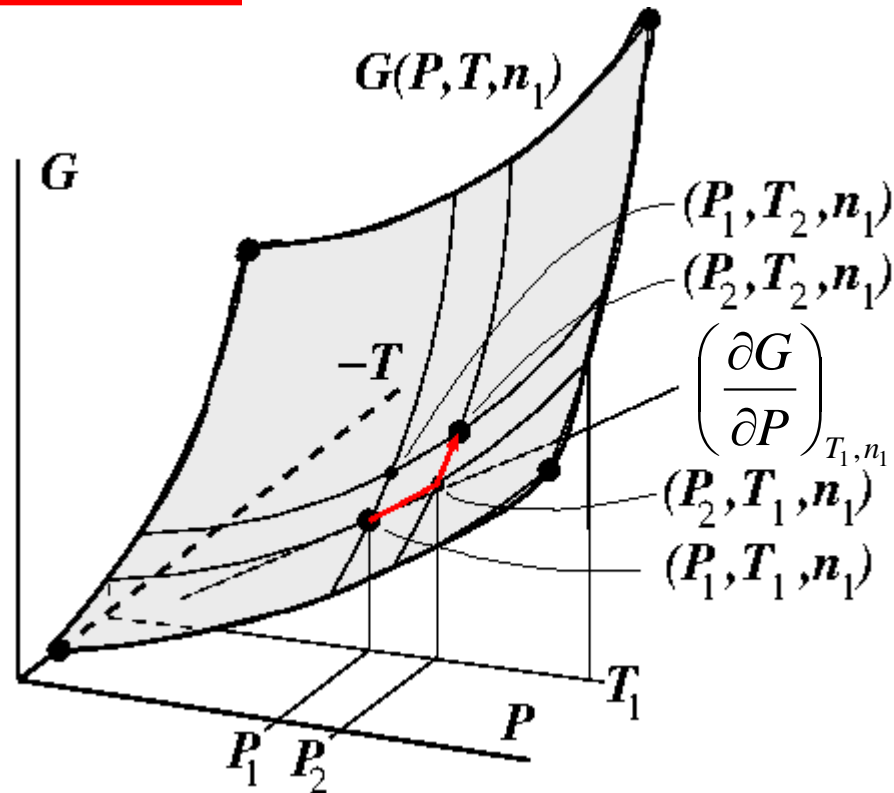
Process: $(P_1, V_1, T_1, n_1) \Rightarrow (P_2, V_2, T_2, n_1)$

Total differential of a state function: G

$$dG = VdP - SdT$$

$$dn = 0$$

(closed system)



V
follows
from the
equation
of state

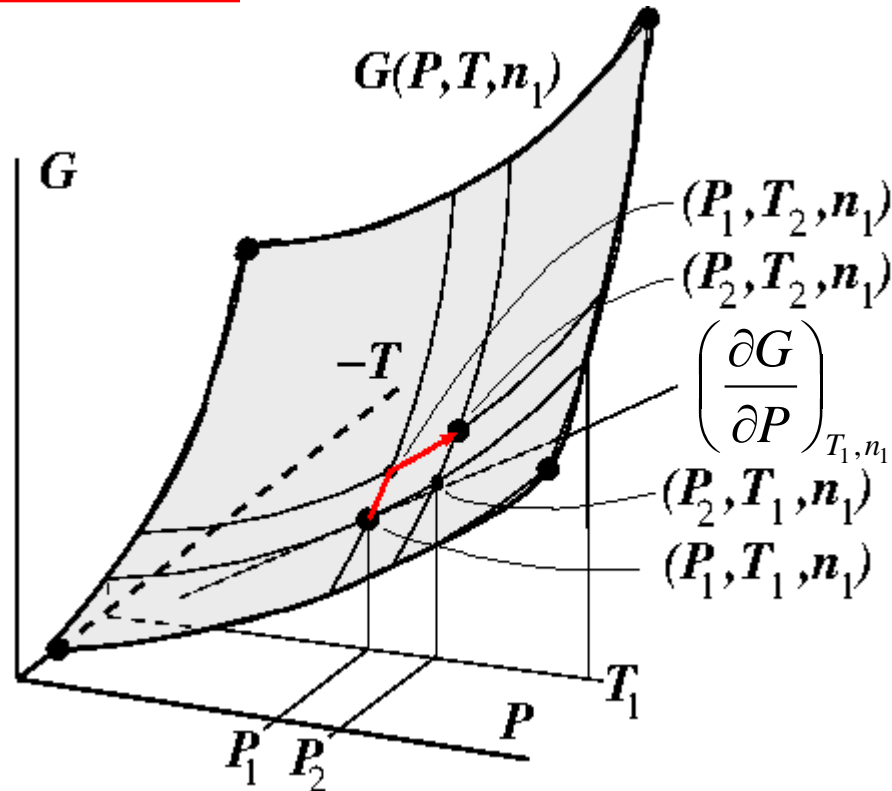
$$\Delta G(P_1, T_1 \rightarrow P_2, T_2) \Big|_n = \int_{P_1}^{P_2} \left(\frac{\partial G}{\partial P}\right)_{T_1, n} dP + \int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_{P_2, n} dT$$

Total differential of a state function: G

$$dG = VdP - SdT$$

$$dn = 0$$

(closed system)



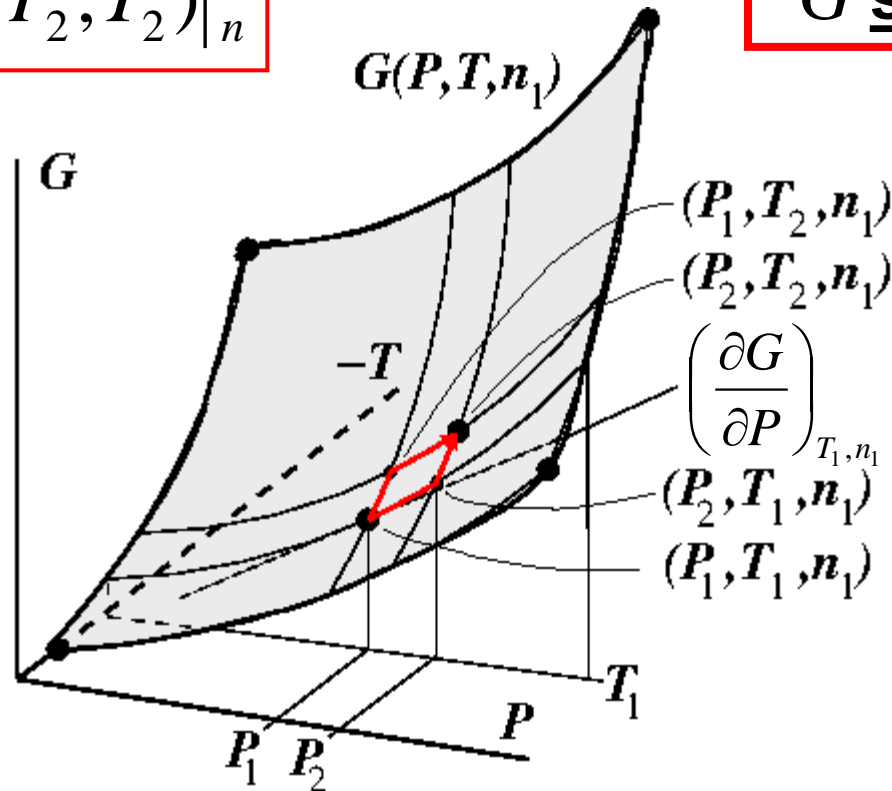
V
follows
from the
equation
of state

$$\Delta G(P_1, T_1 \rightarrow P_2, T_2)|_n = \int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_{P_1, n} dT + \int_{P_1}^{P_2} \left(\frac{\partial G}{\partial P}\right)_{T_2, n} dP$$

Total differential of a state function: G

$$\Delta G(P_1, T_1 \rightarrow P_2, T_2) \Big|_n$$

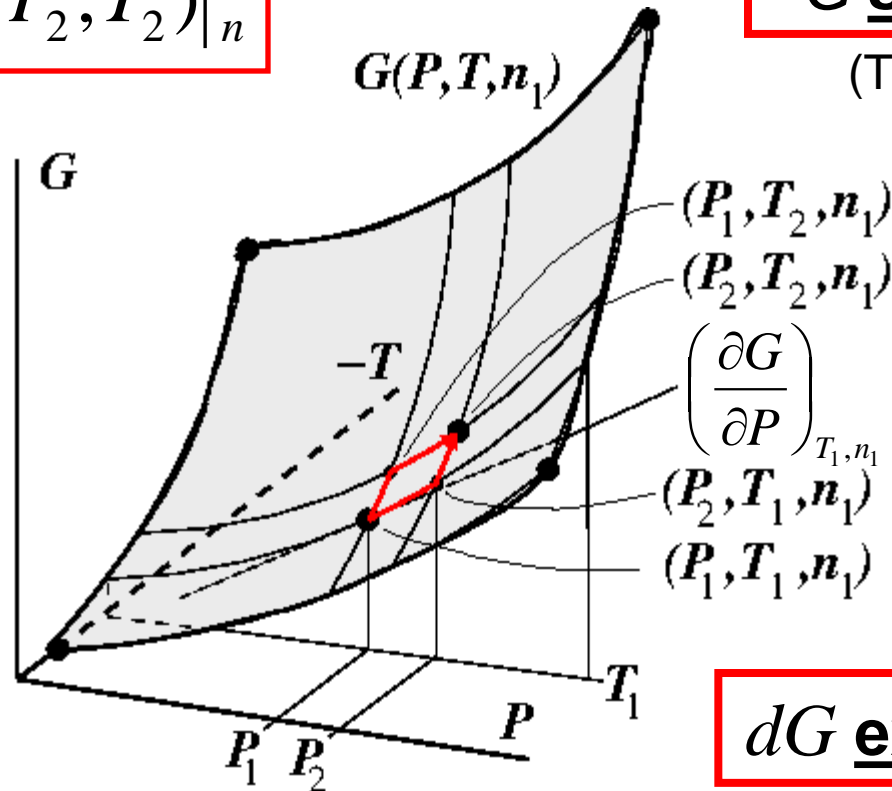
G state function



$$\int_{P_1}^{P_2} \left(\frac{\partial G}{\partial P} \right)_{T_1, n} dP + \int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T} \right)_{P_2, n} dT = \int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T} \right)_{P_1, n} dT + \int_{P_1}^{P_2} \left(\frac{\partial G}{\partial P} \right)_{T_2, n} dP$$

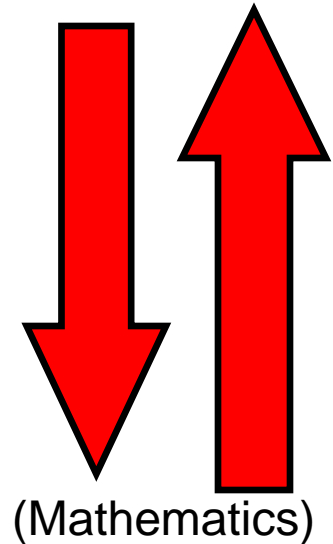
Total differential of a state function: G

$$\Delta G(P_1, T_1 \rightarrow P_2, T_2) \Big|_n$$



G state function

(Thermodynamics)



dG exact differential

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_{T, n} \right)_{P, n} = \left(\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_{P, n} \right)_{T, n}$$

$$\left(\frac{\partial^2 G}{\partial T \partial P} \right) = \left(\frac{\partial^2 G}{\partial P \partial T} \right)$$

Total differential of a state function: G

$$dn = 0$$

Any change in G


$$\Delta G = \int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T} \right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial G}{\partial P} \right)_{T_2} dP$$

Total differential of G

$$dG = \left(\frac{\partial G}{\partial T} \right)_P dT + \left(\frac{\partial G}{\partial P} \right)_T dP$$

Characteristic
(fundamental)
equation of G

$$dG = -SdT + VdP$$


$$S = - \left(\frac{\partial G}{\partial T} \right)_P \text{ and } V = \left(\frac{\partial G}{\partial P} \right)_T$$

Exact differential of a state function: Maxwell relation

$$dG = \left(\frac{\partial G}{\partial T} \right)_P dT + \left(\frac{\partial G}{\partial P} \right)_T dP$$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial^2 G}{\partial T \partial P} \right) = \left(\frac{\partial^2 G}{\partial P \partial T} \right)$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right)_P = \left(\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_P \right)_T$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$\left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T$$

Maxwell relation

General properties of a differentiable function: $f(x,y)$

(See Atkins (ed. 11): The chemist's toolkit 9 (p. 44) or 10 (p. 105))

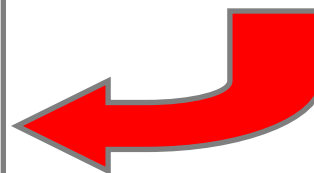
$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right)$$



$$\left(\frac{\partial y}{\partial x}\right)_f \left(\frac{\partial x}{\partial f}\right)_y \left(\frac{\partial f}{\partial y}\right)_x = -1$$

Euler chain relation

$$\left(\frac{\partial y}{\partial x}\right)_f = -\frac{1}{\left(\frac{\partial x}{\partial f}\right)_y \left(\frac{\partial f}{\partial y}\right)_x} = -\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial y}{\partial f}\right)_x$$



Exercise 2

$$\left(\frac{\partial y}{\partial x}\right)_f = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_f}$$

Exact differential of a state function: Maxwell relations

$$dG = -SdT + VdP$$

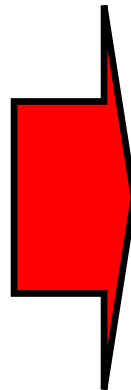


Maxwell relations

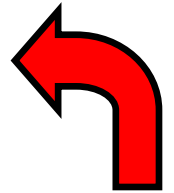
$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$$

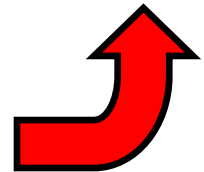


So we can simply determine the change in entropy of a process running at constant T by integrating a more easily measurable quantity $(\partial V/\partial T)_P$ over the pressure change during the process



$$\Delta S|_T = -\int \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dS|_T = -\left(\frac{\partial V}{\partial T}\right)_P dP$$



Exercise 3

Exact differential of a state function: Maxwell relations

$$dG = -SdT + VdP$$



Maxwell relations

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$$

So we can simply determine the change in entropy of a process running at constant T by integrating a more easily measurable quantity $(\partial V/\partial T)_P$ over the pressure change during the process

$$\Delta S|_T = -\int \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dS|_T = -\left(\frac{\partial V}{\partial T}\right)_P dP$$

Exercise 3

