Study Guide Thermodynamics 2, 2025/2026

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 **Thermo 2 website** .

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 - Thermodynamics of mixtures - Thermodynamics of solutions - Activity - Electrolytes - Surface tension - 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 (will be recorded)**
  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 (2024/2025) can be found in the COURSE GUIDE at **dullenslab/teaching** .
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 (this) 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
03/09	2D+3E	3-10,18-19	2D+3D	2.10-11+3.7-8	Recap, Exact diff., Molec. gasses
10/09	4	11-12	4	4	Phase diagr. of pure subst.
17/09	5A+5B.1	13-17	5A-B	5.1-5	P, x-phase diagrams
24/09	5B.1+5C	-	5B-C	5.5-8	T, x-phase diagrams
01/10	5B.2+5D+5E	-	5C-D	5.9+*	$s-l$, ternary phase diagr.
08/10	6+5F	-	6+5F	6+5.13	Electrolytes, Electrochemistry
15/10	14C.2-4+4B.1(c)	20-24	16C.2-4	17.8-10+4.4(c)	Interfaces, Statistical Thermod.

- **Tutorials**
  The tutorial exercises will be available before, and the solutions after, each tutorial on the website: **Thermo 2 website**.
  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; group 1 for the Premaster students and group 2 and 3 for the other students. Students can choose freely which group to join, but room capacity is limited.

Group	cohort	room	day	time	TA
1	Premaster	Transitorium 00.005	Thursday	10:30-12:15	Hugo Meekes
2	Chem., Science, MLS	HG01.028	Thursday	13:30-15:15	Zuzanna Czarnobil
3	Chem., Science, MLS	Transitorium 00.012	Thursday	13:30-15:15	Diya Jiworo

- **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).

Appendix C

ormulae first year course Thermodynamics

$$PV = nRT = NkT$$

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

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W, \quad \text{so} \quad \Delta U = \int \mathrm{d}Q + \int \mathrm{d}W = Q + W$$

$$\mathrm{d}Q|_V = C_V \mathrm{d}T, \quad \text{where} \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\mathrm{d}Q|_P = C_P \mathrm{d}T, \quad \text{where} \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\mathrm{d}S = \frac{\mathrm{d}Q^{rev}}{T} \geq \frac{\mathrm{d}Q}{T}$$

$$\mathrm{d}S_{tot} = \mathrm{d}S + \mathrm{d}S_{surr} \geq 0$$

$$S = k \ln W$$

$$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$H = U + PV$$

$$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$A = U - TS$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$G = H - TS$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

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

$$\Delta_r G^{\ominus} = -RT \ln K \quad \text{with} \quad K = \left(\prod_i a_i^{\nu_i}\right)_{eq}$$

$$\Delta_r G = -\nu F E, \quad \text{so} \quad E = E^{\ominus} - \frac{RT}{\nu F} \ln Q$$

==

$$\mathrm{d}W = -P_{ext.}\mathrm{d}V + \mathrm{d}W' \quad \text{and} \quad \mathrm{d}W'_{max} = (\mathrm{d}G)_{P,T} \quad \text{and} \quad \mathrm{d}W' = E\mathrm{d}q$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_{j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}}$$

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

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$\Delta_{\text{mix}}^{\text{ideal}} S = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

Appendix D

Formulae Thermodynamics 2

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

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

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$P_j = x_j P_j^*$$

$$P_j = y_j P$$

$$P_B = x_B K_B$$

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

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

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

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V}$$

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} \approx \frac{\Delta_{\text{trs}} H}{RT^2}$$

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

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

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

$$F = C - P + 2$$

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

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

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

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

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

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

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

Appendix B

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 ($P, V, T, n, \cdots$) 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 ($\mathrm{d}T = 0$ for the system).

Isobaric process A process that proceeds at constant pressure ($\mathrm{d}P = 0$ for the system).

Isochoric process A process that proceeds at constant volume ($\mathrm{d}V = 0$ for the system).

Adiabatic process A process that proceeds without heat exchange with the environment ($\mathrm{d}Q = 0$).

Isolated system No exchange between system and surroundings ($\mathrm{d}W = \mathrm{d}Q = \mathrm{d}n = 0$).

Closed system No exchange of matter between system and surroundings ($\mathrm{d}n = 0$); there can be exchange of work ($\mathrm{d}W \neq 0$) or heat ($\mathrm{d}Q \neq 0$).

Open system A non-closed system ($\mathrm{d}n \neq 0$).

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.

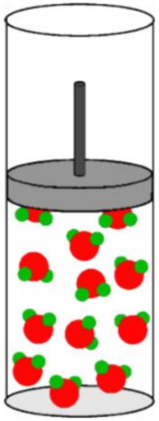
Intensive quantity Does not change if we enlarge the system; e.g. T and P.

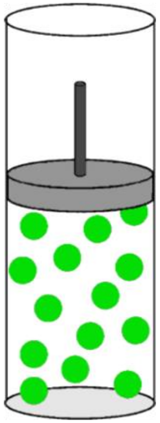
Extensive quantity Doubles if we make the system twice as large; e.g. V and n.

Statistical thermodynamics Relates microscopic processes and (macroscopic) thermodynamics.

Lecture 1

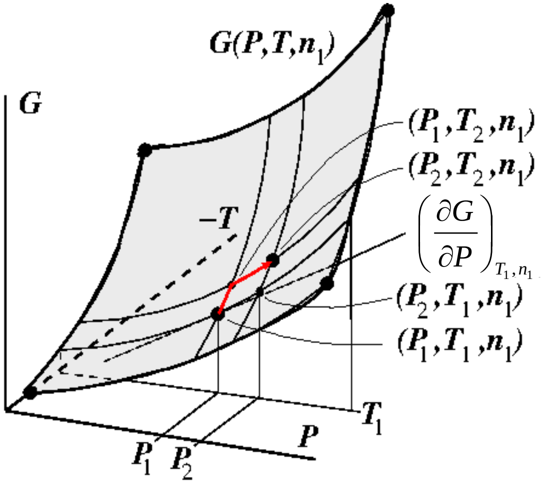
- **Molecular (perfect) gases *vs* atomic gases**

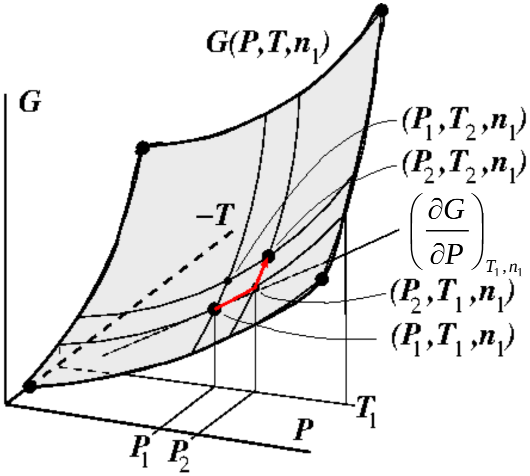




- **Total differential of (thermodynamic) functions**

(including a recap of thermodynamics 1)



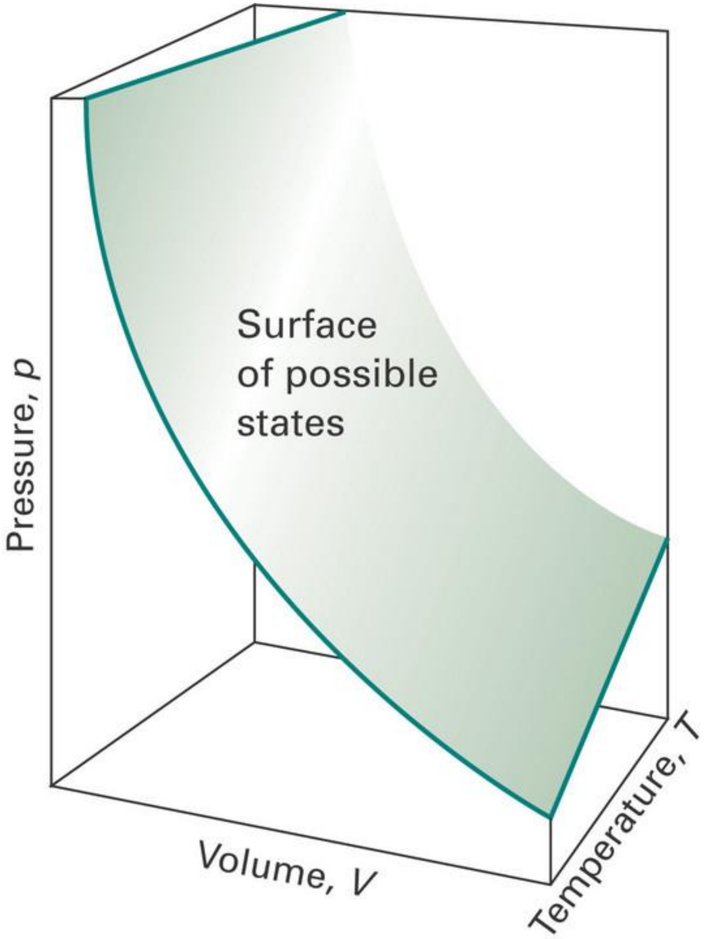


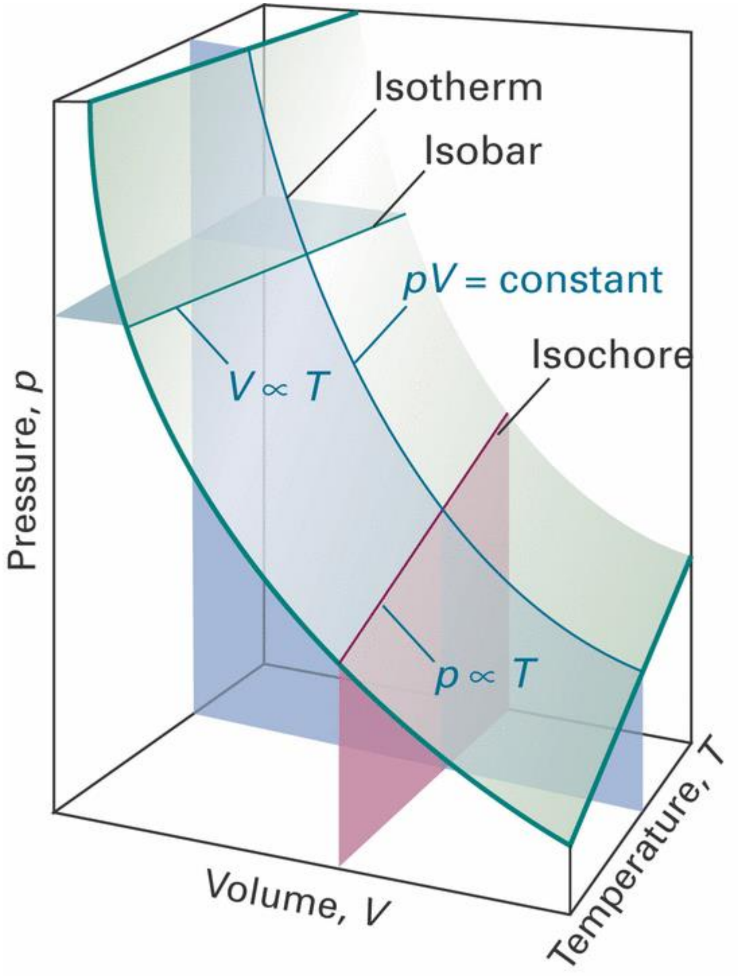
Lecture 1

- **Molecular (perfect) gases *vs* atomic gases**

- **Total differential of (thermodynamic) functions**

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



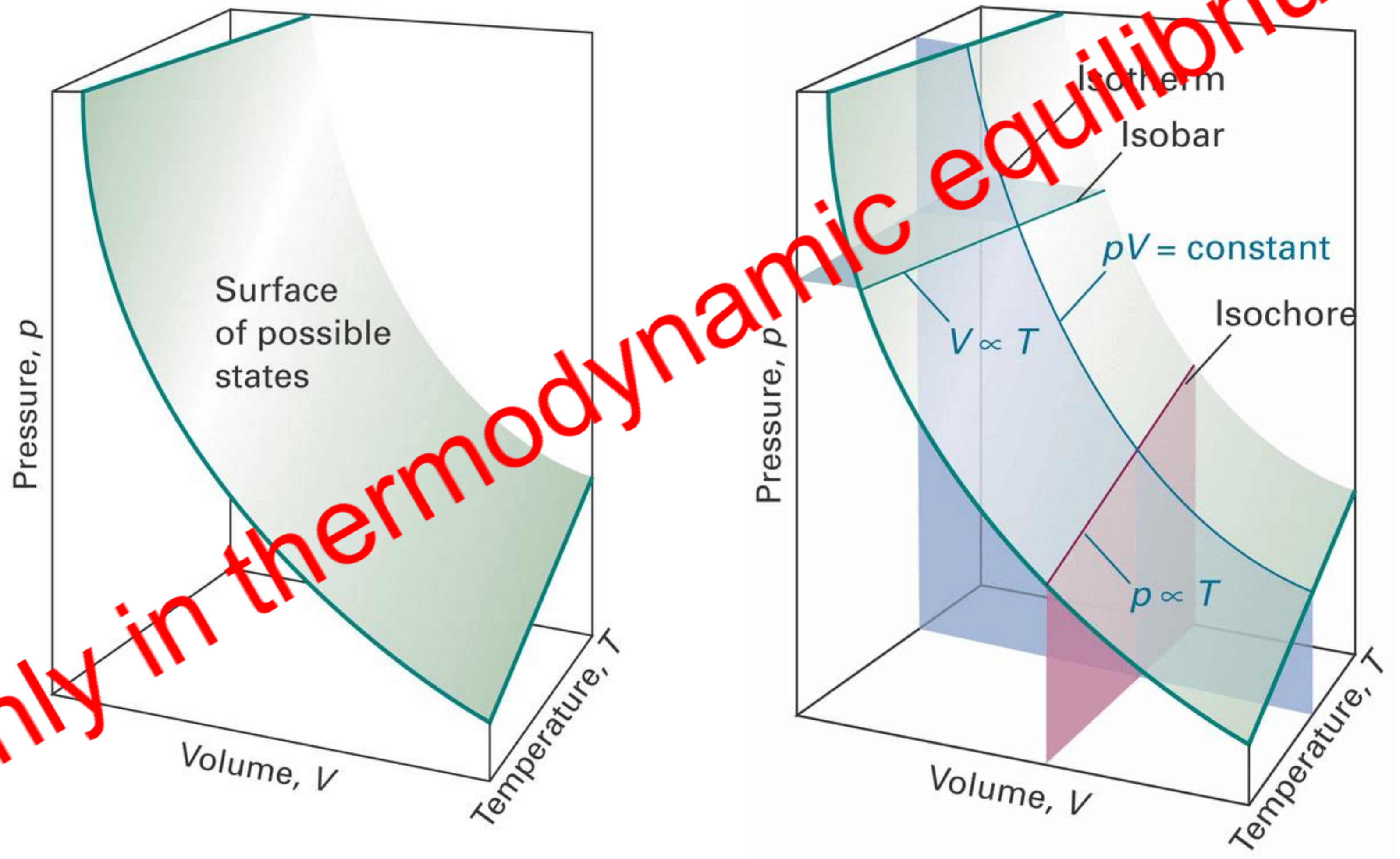


Closed system: n constant ($\mathrm{d}n = 0$)

(=> 4 variables reduced to 3)

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

Only in thermodynamic equilibrium!



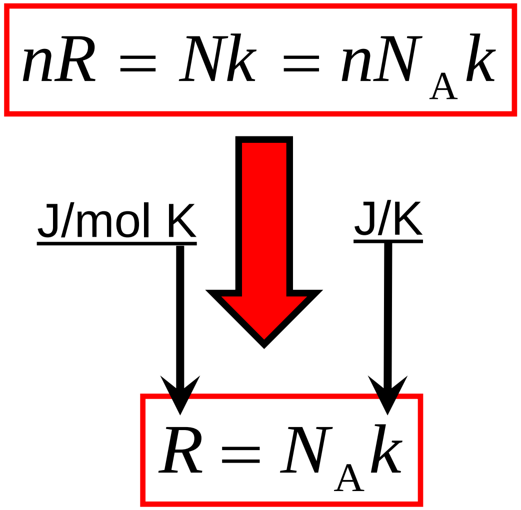
Closed system: n constant ($dn = 0$)

(=> 4 variables reduced to 3)

Amadeo Avogadro

1776-1856

$$N_A = 6.02214\ldots \cdot 10^{23}\,\mathrm{mol}^{-1}$$



$$nR = Nk = nN_A k$$

J/mol K

J/K

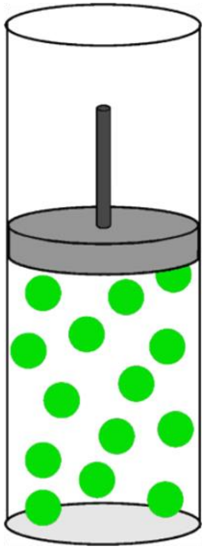
$$R = N_A k$$

Ludwig Boltzmann

1844-1906

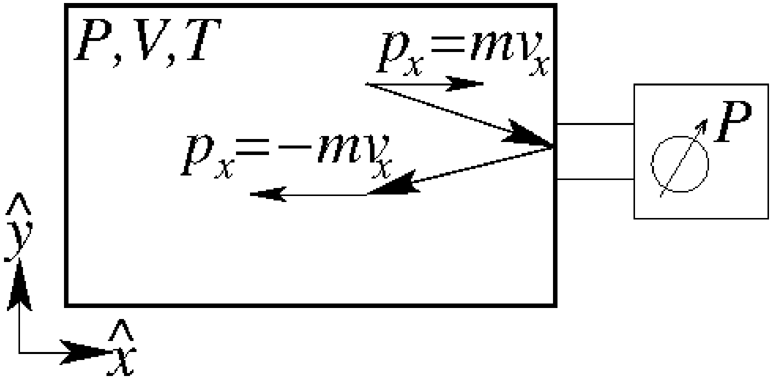
$$k = 1.3806\ldots \cdot 10^{-23}\,JK^{-1}$$

Perfect gas: from atoms to molecules



Atomic perfect gas

$$\boxed{PV = nRT}$$

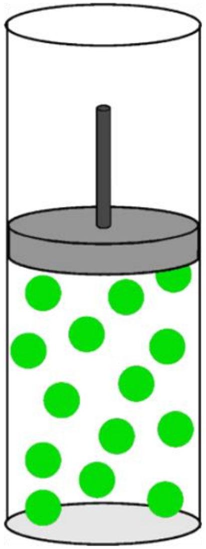


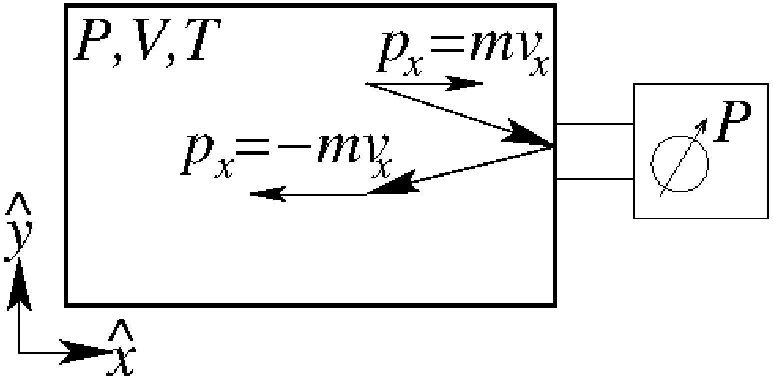
(Study guide p.3-4)

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

Internal energy of the system

Perfect gas: from atoms to molecules





(Study guide p.3-4)

Atomic perfect gas

$$\boxed{PV = nRT}$$

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

Internal energy of the system

Only for atomic perfect gas!

Perfect gas: from atoms to molecules

(Study guide p.17-18)

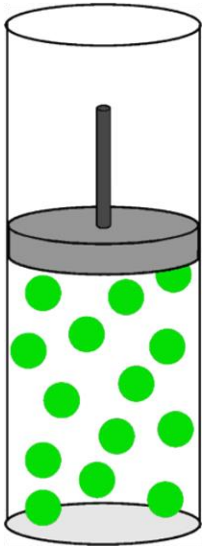
$$\boxed{U = \frac{1}{2}kT}$$

equipartition theorem

(from statistical thermod.)

Internal energy

per degree of freedom



Atomic perfect gas

$$\boxed{PV = nRT}$$

$$\boxed{U = 3N\frac{1}{2}kT} \xrightarrow[Nk = nR]{} \boxed{U = \frac{3}{2}nRT}$$

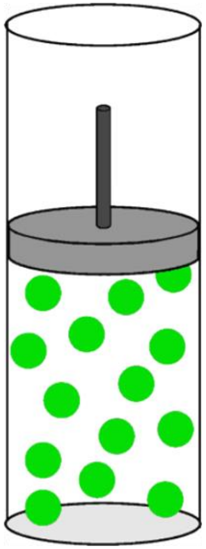
(*x*,*y*,*z*) **(*N* atoms)**

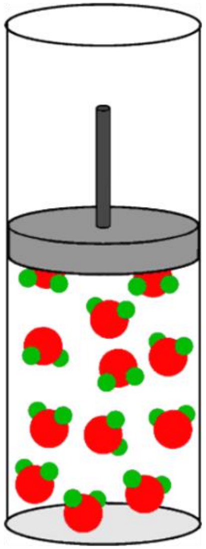
3*N* degrees of freedom

Perfect gas: from atoms to molecules

Only Translational degrees of freedom

Also Rotational and Vibrational degrees of freedom





Atomic perfect gas

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

$$\boxed{N_{\mathrm{T}} = 3}$$

Molecular perfect gas

$$\boxed{N_{\mathrm{R}} = ?}$$

$$\boxed{N_{\mathrm{V}} = ?}$$

Perfect gas: from atoms to molecules

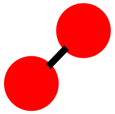
Rotational

degrees of freedom

atom

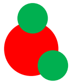
$$\boxed{N_{\mathrm{R}} = 0}$$

linear



$$\boxed{N_{\mathrm{R}} = 2}$$

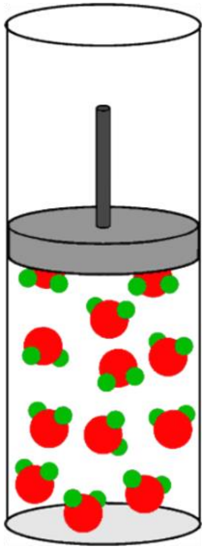
non-linear



$$\boxed{N_{\mathrm{R}} = 3}$$

$$\boxed{U^{\mathrm{R}} = MN_{\mathrm{R}}\frac{1}{2}kT}$$

(M molecules) (N_{R} = # Rotation axes)



Molecular perfect gas

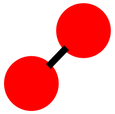
Perfect gas: from atoms to molecules

Rotational degrees of freedom

atom

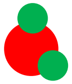
$$\boxed{N_{\mathrm{R}} = 0}$$

linear



$$\boxed{N_{\mathrm{R}} = 2}$$

non-linear



$$\boxed{N_{\mathrm{R}} = 3}$$

$$\boxed{U^{\mathrm{R}} = MN_{\mathrm{R}}\frac{1}{2}kT}$$

Vibrational degrees of freedom

In total: N atoms in M molecules

$3N$ degrees of freedom

$$\boxed{3N = N_{\mathrm{T}}M + N_{\mathrm{R}}M + N_{\mathrm{V}}M}$$

$$\boxed{3N = 3M + N_{\mathrm{R}}M + N_{\mathrm{V}}M}$$

Perfect gas: from atoms to molecules

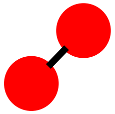
Rotational degrees of freedom

Vibrational degrees of freedom

atom

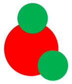
$N_{\mathrm{R}} = 0$ → $N_{\mathrm{V}} = 0$

linear



$N_{\mathrm{R}} = 2$ → $N_{\mathrm{V}} = 3N_{\mathrm{m}} - 5$

non-linear



$N_{\mathrm{R}} = 3$ → $N_{\mathrm{V}} = 3N_{\mathrm{m}} - 6$

N_{m}: # atoms/molecule

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

$$N_{\mathrm{m}} \equiv \frac{N}{M}$$

$$3N = 3M + N_{\mathrm{R}}M + N_{\mathrm{V}}M$$

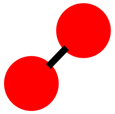
$$N_{\mathrm{V}} = 3\frac{N}{M} - 3 - N_{\mathrm{R}}$$

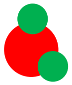
Perfect gas: from atoms to molecules

Rotational degrees of freedom

Vibrational degrees of freedom

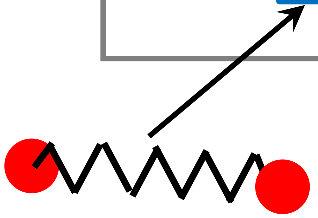
atom  $N_{\mathrm{R}} = 0$ $\Rightarrow$ $N_{\mathrm{V}} = 0$

linear  $N_{\mathrm{R}} = 2$ $\Rightarrow$ $N_{\mathrm{V}} = 3N_{\mathrm{m}} - 5$

non-linear  $N_{\mathrm{R}} = 3$ $\Rightarrow$ $N_{\mathrm{V}} = 3N_{\mathrm{m}} - 6$

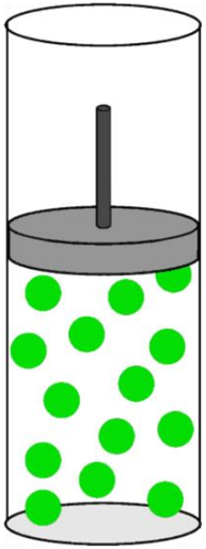
Vibrational energy

$$U^{\mathrm{V}} = \boxed{2} M N_{\mathrm{V}} \frac{1}{2} kT$$



Chemical bond: kinetic and potential energy

Perfect gas: from atoms to molecules



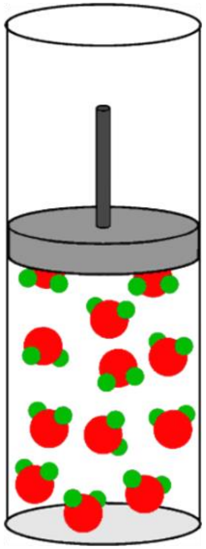
(Study guide p.17-18)

Perfect gas

$$\boxed{PV = nRT}$$

obeys the equipartition theorem

(high T and low P)



Atomic perfect gas

Molecular perfect gas

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

Exercise 1

$$\boxed{U = (3 + N_{\mathrm{R}} + 2N_{\mathrm{V}})\frac{1}{2}MkT}$$

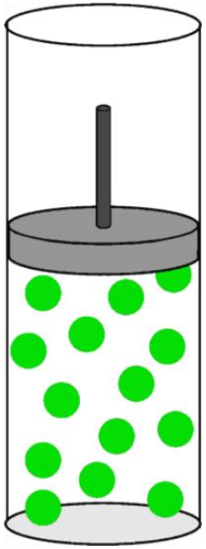
$$\boxed{Nk = nR}$$

$$\boxed{Mk = nR}$$

$$\boxed{C_V = \frac{3}{2}nR} \leftarrow \boxed{C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V} \rightarrow \boxed{C_V = (3 + N_{\mathrm{R}} + 2N_{\mathrm{V}})\frac{1}{2}nR}$$

Perfect gas: from atoms to molecules

(Study guide p.17-18)

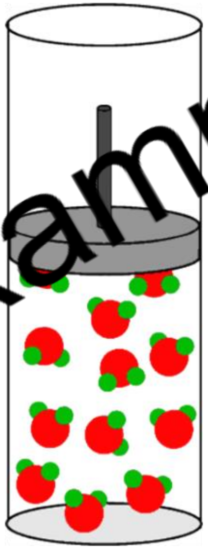


Perfect gas

$$\boxed{PV = nRT}$$

obeys the equipartition theorem

(high T and low P)



Let's work out an example

Atomic perfect gas

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

$$Nk = nR$$

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

Exercise 1

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

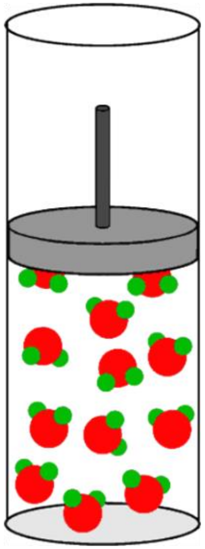
Molecular perfect gas

$$U = \left(3 + N_{\mathrm{R}} + 2N_{\mathrm{V}}\right)\frac{1}{2}MkT$$

$$Mk = nR$$

$$C_V = \left(3 + N_{\mathrm{R}} + 2N_{\mathrm{V}}\right)\frac{1}{2}nR$$

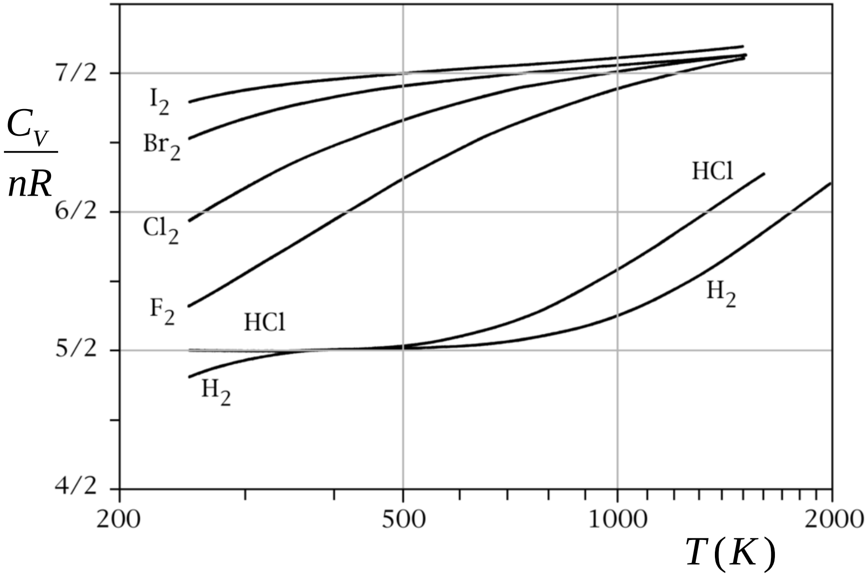
Perfect gas of molecules: example H_2O



$$\boxed{U = \left(3 + N_{\mathrm{R}} + 2N_{\mathrm{V}}\right)\frac{1}{2}MkT = \frac{12}{2}MkT = \frac{12}{2}nRT}$$

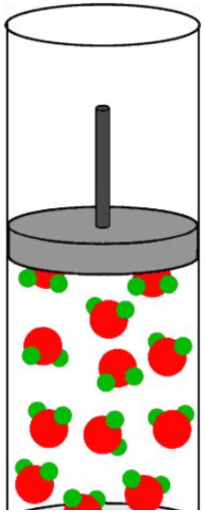
$$\boxed{C_V = \frac{12}{2}nR}$$

cf Argon: $\boxed{C_V^{\mathrm{Ar}} = \frac{3}{2}nR}$



Source: https://en.wikipedia.org/wiki/Molar_heat_capacity

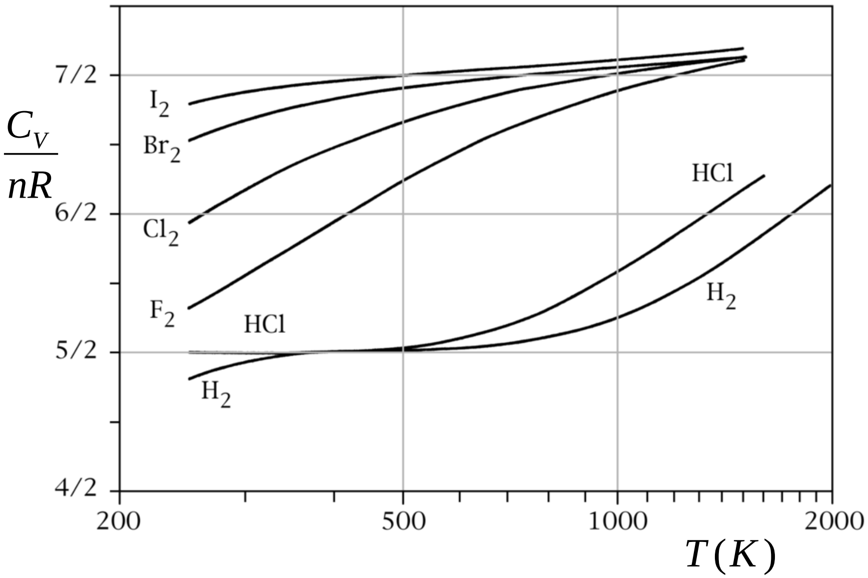
Perfect gas of molecules: example H_2O

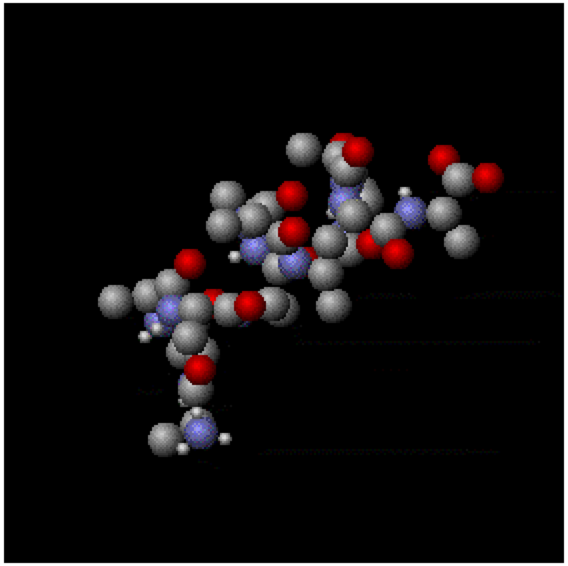


$$\boxed{U = \left(3 + N_\mathrm{R} + 2N_\mathrm{V}\right)\frac{1}{2}MkT = \frac{12}{2}MkT = \frac{12}{2}nRT}$$

$$\boxed{C_V = \frac{12}{2}nR}$$

cf Argon: $\boxed{C_V^{\mathrm{Ar}} = \frac{3}{2}nR}$





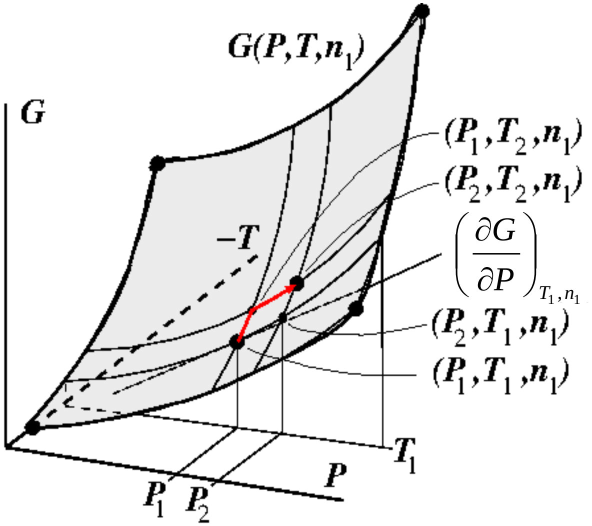
Source: https://en.wikipedia.org/wiki/Molar_heat_capacity

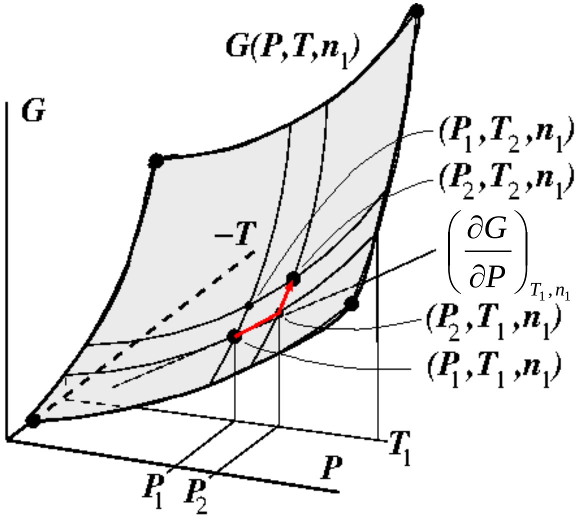
Lecture 1

- Molecular (perfect) gases *vs* atomic gases

- **Total differential of (thermodynamic) functions**

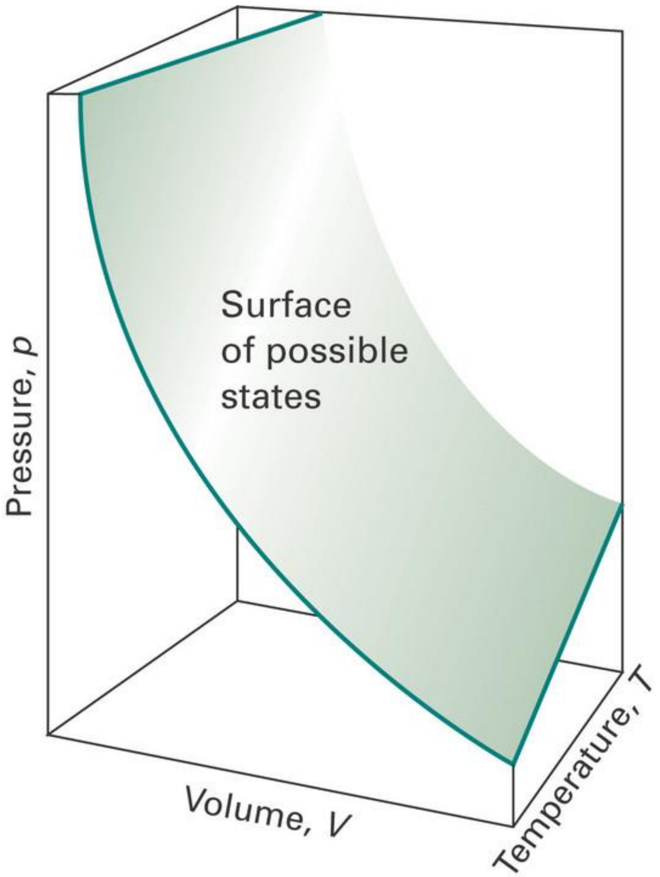
(including a recap of thermodynamics 1)

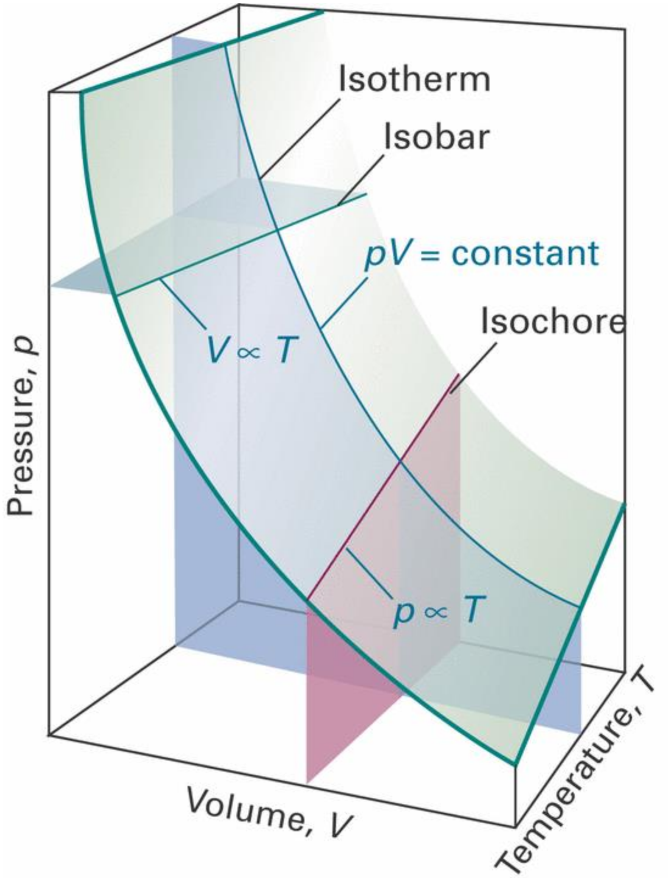




Perfect gas: $PV = nRT = NkT$ (equation of state)

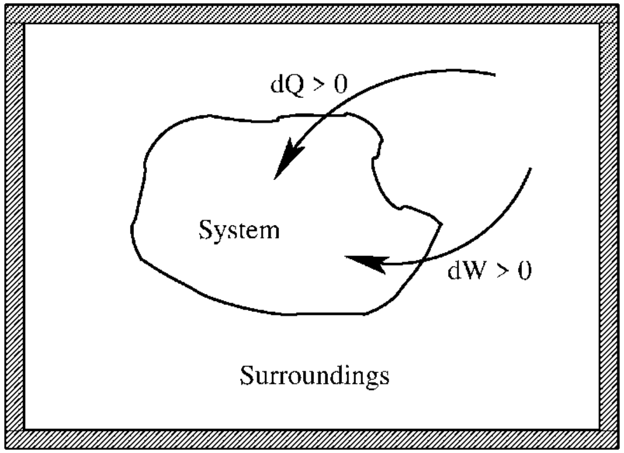
Only for the system in equilibrium





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

General case: equilibrium thermodynamics

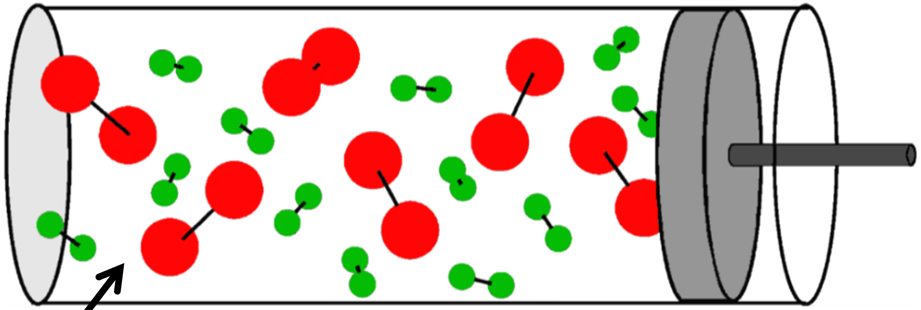


$$\underline{\text{process}}\begin{cases}\boxed{Q = \text{heat}}\\ \boxed{W = \text{work}}\end{cases}$$

(Study guide p.5-10)

Irreversible processes: non-equilibrium and spontaneous

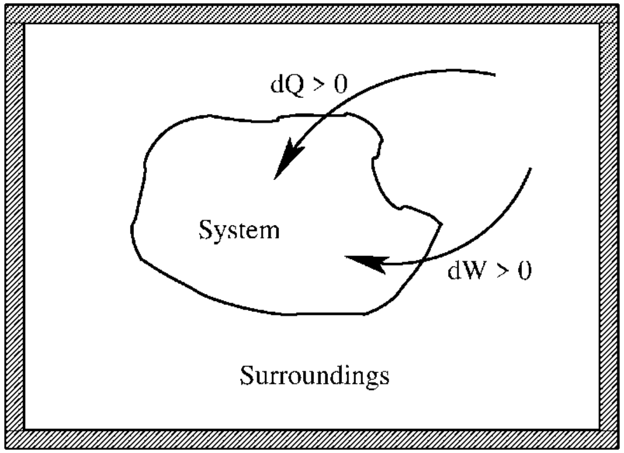
$$\Rightarrow \boxed{Q, W \text{ complicated}} \qquad \boxed{dW = -P_{\text{ext}}\, dV}$$



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

$\boxed{P = ?}$

General case: equilibrium thermodynamics



$$\text{process}\begin{cases} \boxed{Q = \text{heat}} \\ \boxed{W = \text{work}} \end{cases}$$

(Study guide p.5-10)

Irreversible processes: non-equilibrium and spontaneous

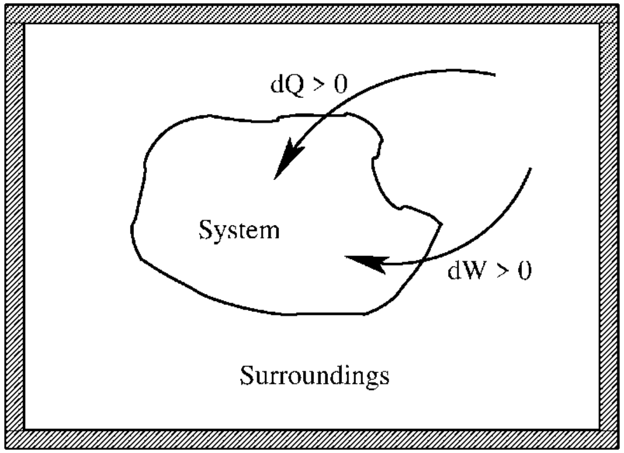
⇒ $\boxed{Q, W \text{ complicate d}}$ $\boxed{dW = -P_{\text{ext}}\, dV}$

Reversible processes: always equilibrium and not spontaneous

$$\Rightarrow \begin{cases} \boxed{dW^{\text{rev}} = -P\,dV} \\ \boxed{dQ^{\text{rev}} = T\,dS} \end{cases}$$

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

General case: equilibrium thermodynamics



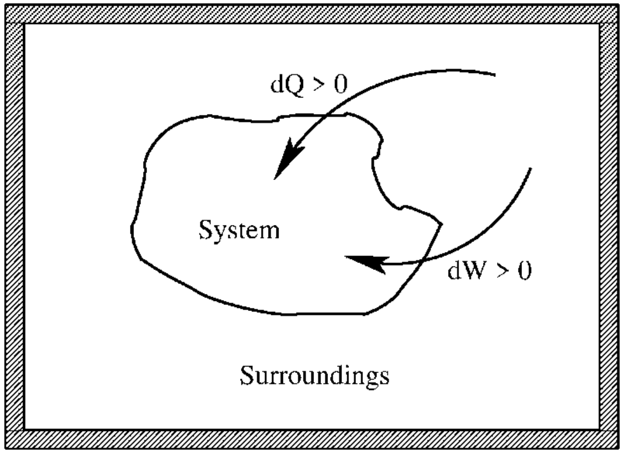
First law:

$$\left.\begin{array}{l}\boxed{dU = dQ + dW}\\[1em] \boxed{dU^{\mathrm{irr}} = dU^{\mathrm{rev}}}\end{array}\right\}$$

$$\Rightarrow \boxed{dU = \underbrace{dQ + dW}_{\text{irreversible}} = \underbrace{TdS - PdV}_{\text{reversible}}}$$

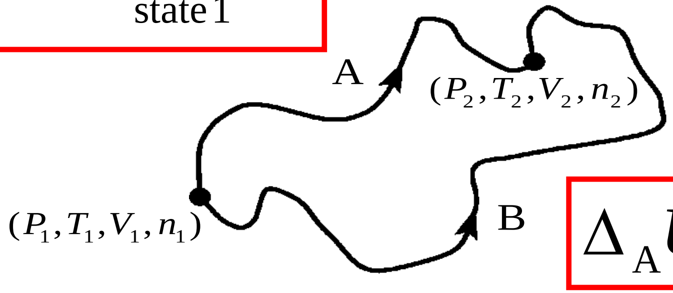
entropy $$\boxed{dS \equiv \frac{dQ^{\mathrm{rev}}}{T}}$$

General case: equilibrium thermodynamics



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

U is a state function



$$\boxed{\Delta_A U = \Delta_B U}$$

$$dU = \underbrace{dQ + dW}_{\text{irreversible}} = \underbrace{TdS - PdV}_{\text{reversible}}$$

First law

dU for an irreversible process can be determined by an alternative reversible process between the same states

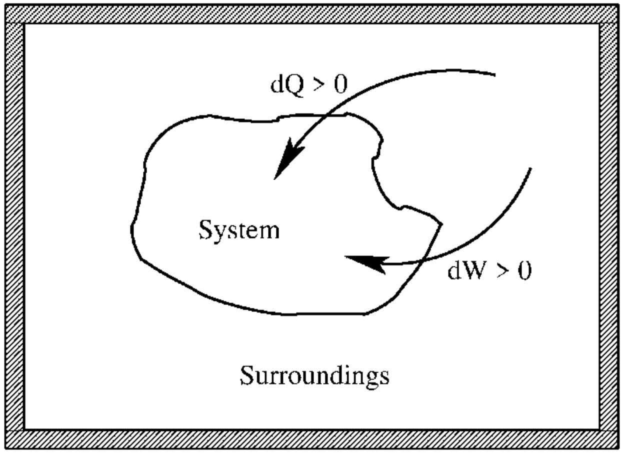
entropy $$\boxed{dS \equiv \frac{dQ^{\text{rev}}}{T}}$$

General case: equation of state

$$\boxed{P = P(V, T, n)}$$

Only for the system in equilibrium

→ only three independent variables



$$\boxed{P, V, T, n}$$

are the state variables of the system

For a closed system: n constant ($\mathrm{d}n = 0$)

→ only two independent variables

Total differential of a state function: *U*

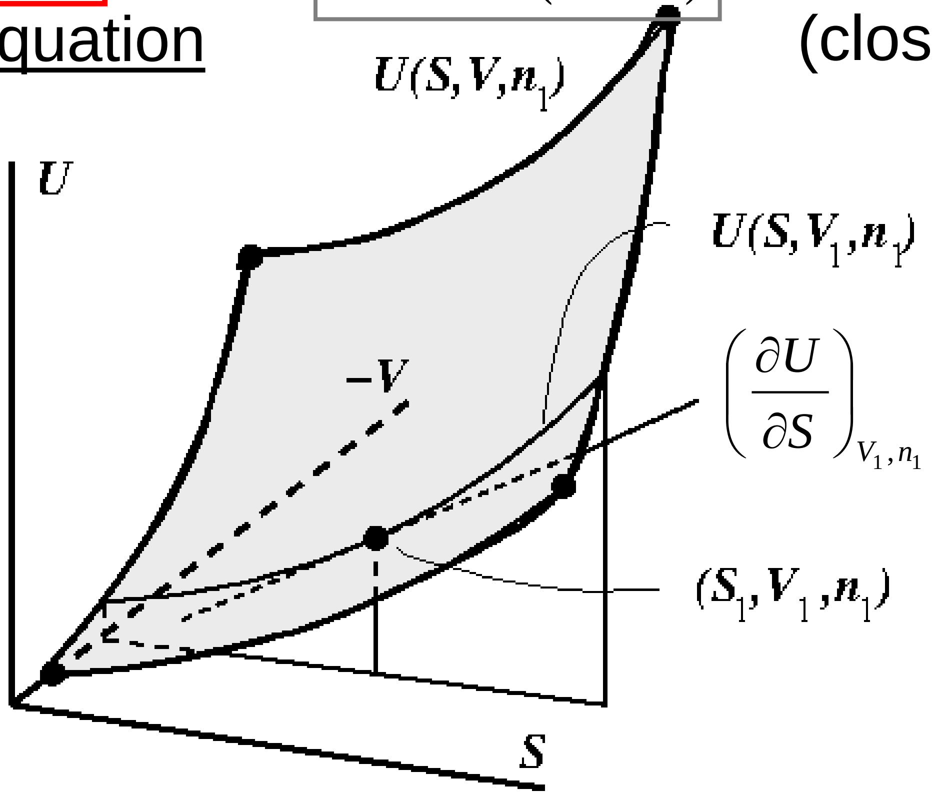
$$\boxed{dU = TdS - PdV}$$

characteristic equation

$$\boxed{U = U(S,V)}$$

$$\boxed{dn = 0}$$

(closed system)



First law:

$$\boxed{dU = dQ + dW}$$

at constant volume:

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

Total differential of a state function: *U*

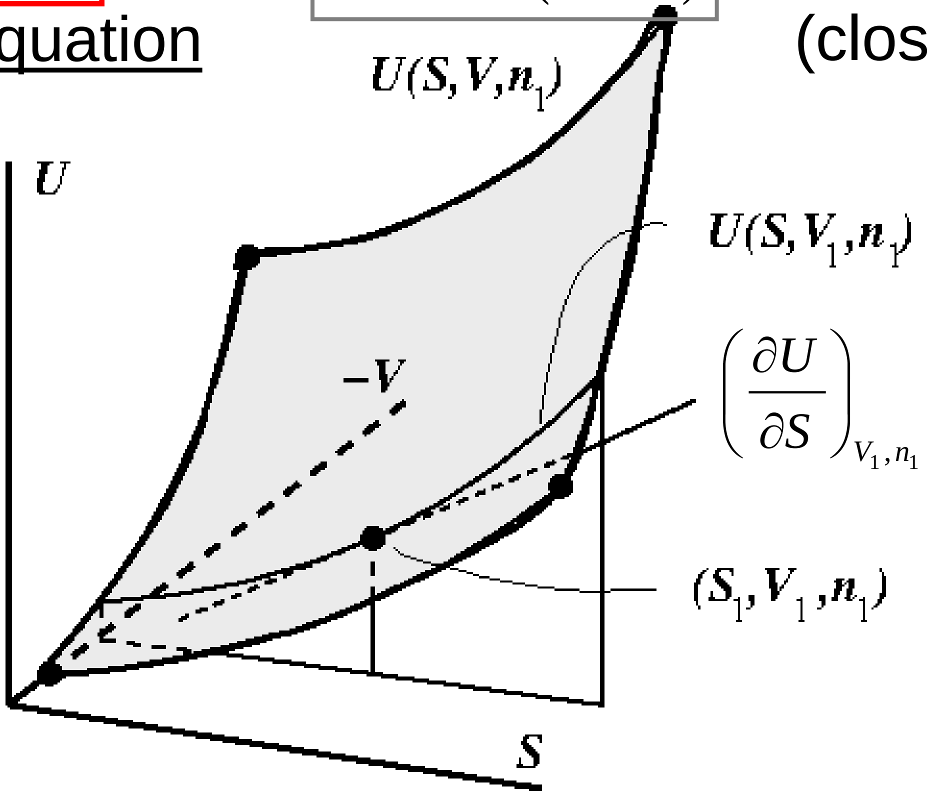
$$\boxed{dU = TdS - PdV} \Rightarrow \boxed{U = U(S,V)}$$

characteristic equation

$$\boxed{dn = 0}$$

(closed system)

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



at constant volume:

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

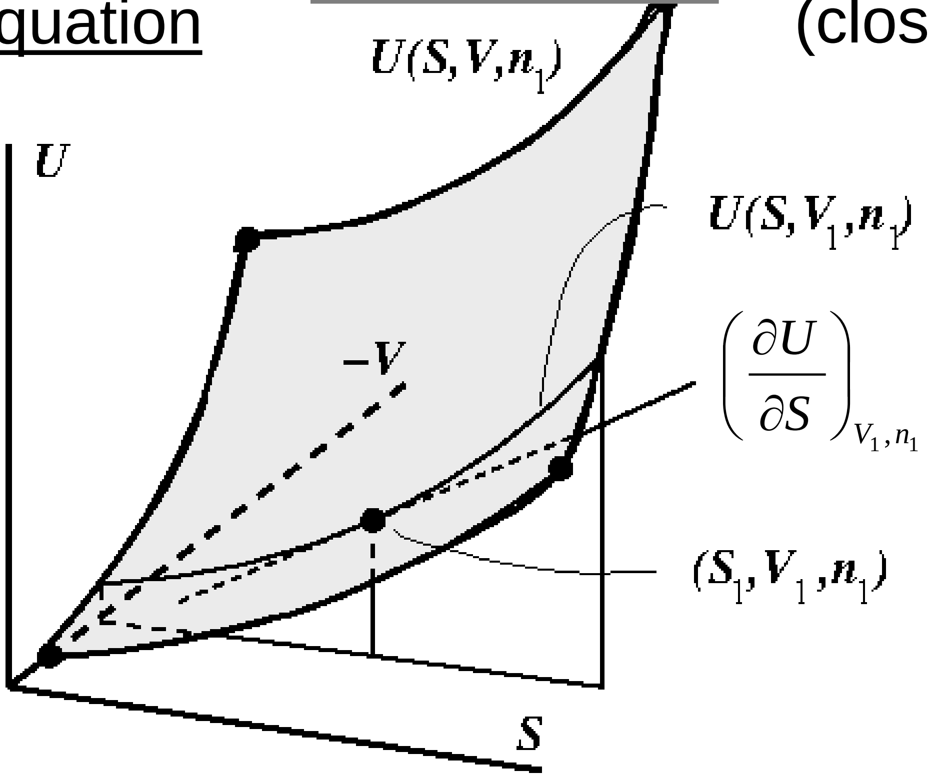
Total differential of a state function: *U*

$$\boxed{dU = TdS - PdV} \Rightarrow \boxed{U = U(S,V)}$$

characteristic equation

$$\boxed{dn = 0}$$

(closed system)



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

at constant volume:

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

Total differential of a state function: *U*

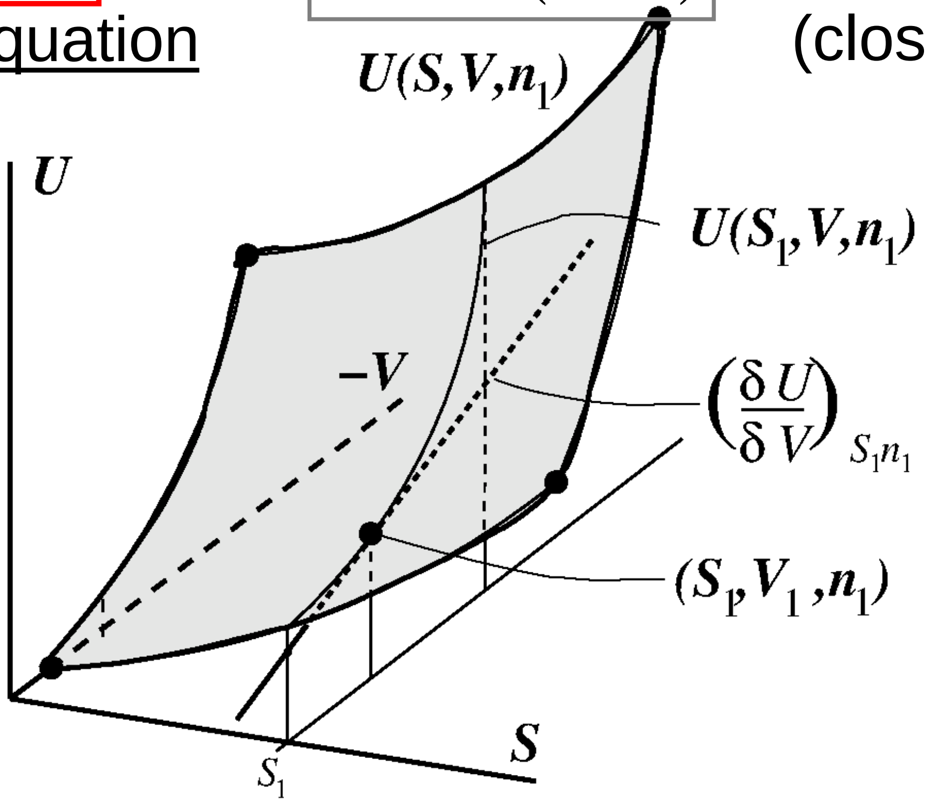
$$\boxed{dU = TdS - PdV} \Rightarrow \boxed{U = U(S,V)}$$

characteristic equation

$$\boxed{dn = 0}$$

(closed system)

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_{S,n} = -P}$$



at constant entropy:

$$\boxed{dU\Big|_{S,n} = \left(\frac{\partial U}{\partial V}\right)_{S,n} dV = -PdV} \Rightarrow \boxed{\Delta U\Big|_{S,n} = -\int PdV}$$

Total differential of a state function: U

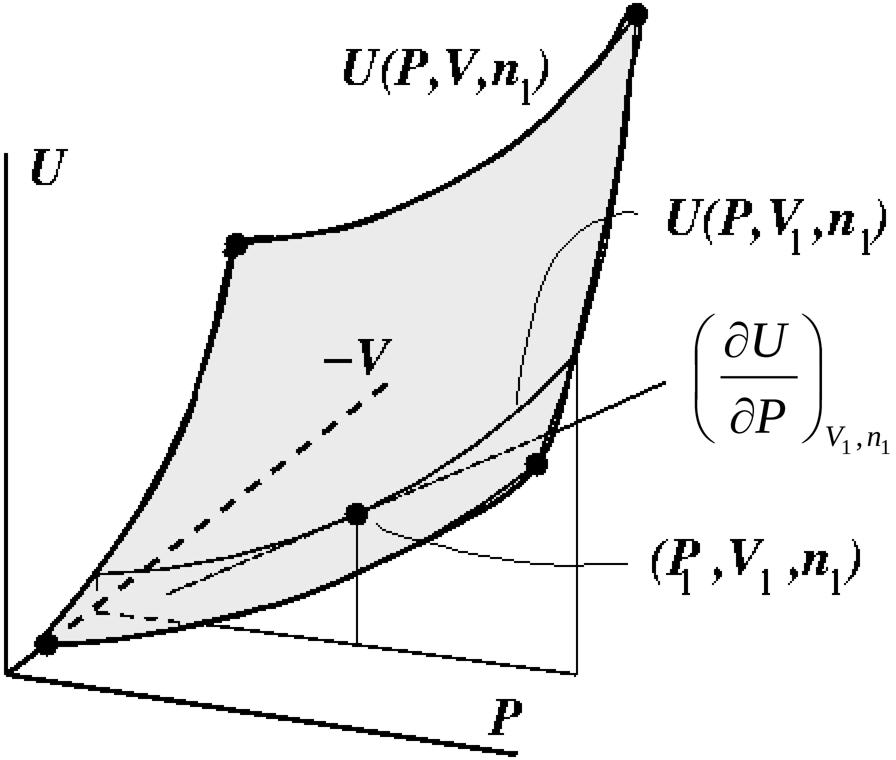
(SG: appendix A)

$$\boxed{dn = 0}$$

(closed system)

Alternatively:

Choose
P and V
as
independent
variables



T
follows
from the
equation
of state

at constant volume:

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

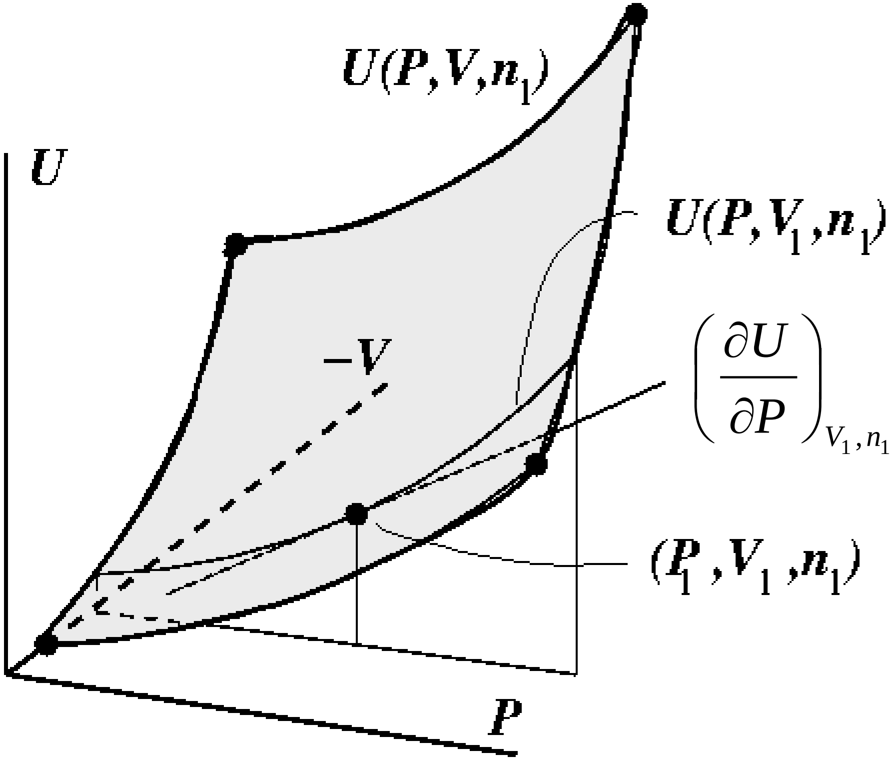
$$\boxed{\Delta U\Big|_{V,n} = \int \left(\frac{\partial U}{\partial P}\right)_{V,n} dP}$$

Total differential of a state function: *U*

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

$\boxed{dn = 0}$

(closed system)



T follows from the equation of state

dP is not the most convenient variable for dU

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

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

Introduce new energy function: Enthalpy *H*

Solution for using P as a variable: (SG: page 6)

define Enthalpy H

$$\boxed{H \equiv U + PV}$$

$$\boxed{dH = dU + PdV + VdP = TdS - PdV + PdV + VdP}$$

$$\boxed{dH = TdS + VdP} \Rightarrow \boxed{H = H(S,P)}$$

Consequence: heat capacity differs for *U* and *H*

$$\boxed{dU \equiv dQ + dW \underset{\uparrow}{=} dQ - PdV} \Rightarrow \boxed{C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

(equilibrium)

$$\boxed{dH \equiv TdS + VdP = dQ + VdP} \Rightarrow \boxed{C_P \equiv \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

Introduce new energy function: Enthalpy *H*

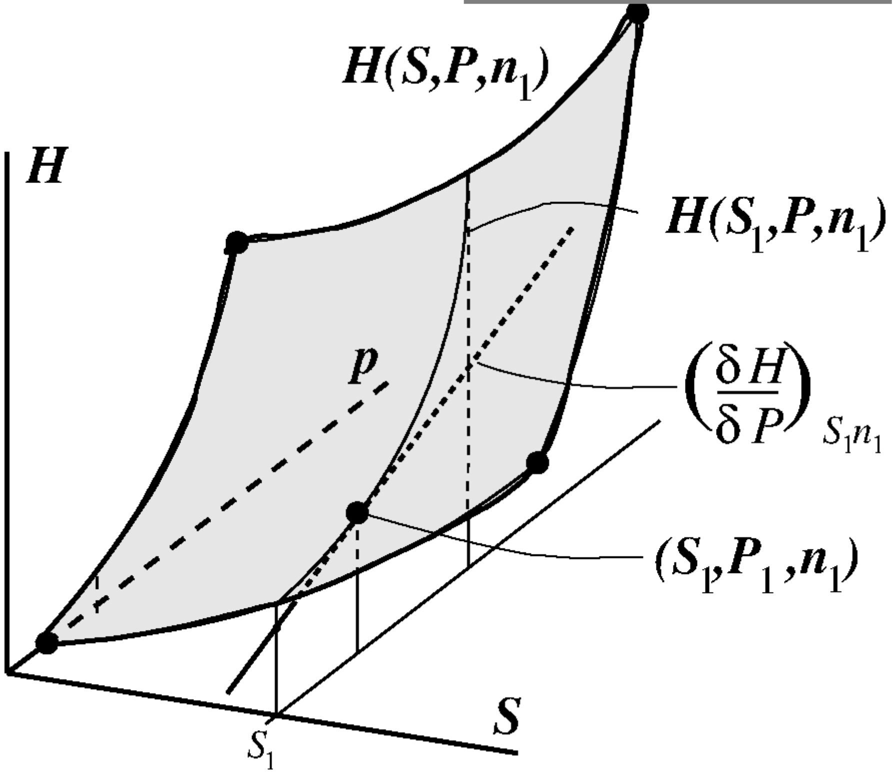
$$\boxed{dH = TdS + VdP} \Rightarrow \boxed{H = H(S,P)}$$

$$\boxed{dn = 0}$$

(closed system)

So enthalpy:

If you further do not like entropy *S* as independent variable



T follows from the equation of state

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

$$\boxed{\Delta H\Big|_{S,n} = \int V\,dP}$$

Helmholtz free energy and Gibbs free energy

(SG: page 8-10)

…then define Helmholtz free energy A

$$\boxed{A \equiv U - TS}$$

$$\boxed{dA = dU - TdS - SdT = TdS - PdV - TdS - SdT}$$

$$\Rightarrow \boxed{dA = -PdV - SdT} \Rightarrow \boxed{W_{\text{delivered}}^{\text{max}} = \Delta A\big|_T}$$

…and the Gibbs free energy G defined via the enthalpy H

$$\boxed{G \equiv H - TS} \qquad \boxed{dH = TdS + VdP}$$

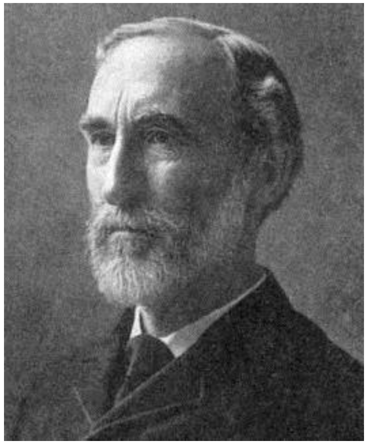
$$\boxed{dG = dH - TdS - SdT = TdS + VdP - TdS - SdT}$$

$$\Rightarrow \boxed{dG = VdP - SdT} \Rightarrow \boxed{W_{\text{delivered}}^{\text{'max}} = \Delta G\big|_{P,T}}$$

Total differential of a state function: Choose appropriate energy function

$$\left.\begin{aligned}
&\textbf{For a choice } S \textbf{ and } V\textbf{ :} && \boxed{dU = TdS - PdV}\\
&\textbf{For a choice } S \textbf{ and } P\textbf{ :} && \boxed{dH = TdS + VdP}\\
&\textbf{For a choice } V \textbf{ and } T\textbf{ :} && \boxed{dA = -PdV - SdT}\\
&\textbf{For a choice } \underbrace{P \textbf{ and } T}_{\textbf{your favourite state variables}}\textbf{ :} && \boxed{dG = VdP - SdT}
\end{aligned}\right\}\ \boxed{\underline{\textbf{Characteristic equations}}}$$

Herman von Helmholtz
1821-1894



Josiah Gibbs
1839-1903

Total differential of a state function: Choose appropriate energy function

For a choice S and V : $\boxed{dU = TdS - PdV}$

For a choice S and P : $\boxed{dH = TdS + VdP}$

For a choice V and T : $\boxed{dA = -PdV - SdT}$

For a choice $\underbrace{P \text{ and } T}_{\text{your favourite state variables}}$: $\boxed{dG = VdP - SdT}$

Characteristic equations

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

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

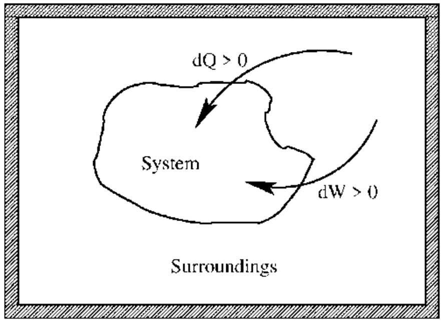
General case: equilibrium thermodynamics

Second law: for a spontaneous process the total entropy S_{tot} always increases

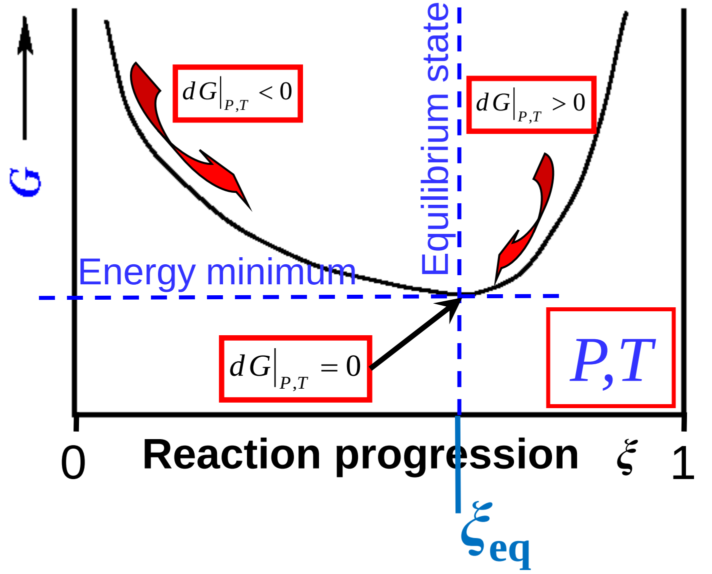
$$dS_{\text{tot}} = dS + dS_{\text{surr}} > 0$$

Second law: in thermodynamic equilibrium $dS_{\text{tot}} = 0$

$$dS^{\text{eq}}_{\text{tot}} = dS + dS_{\text{surr}} = 0$$



$$dG^{\text{eq}}\Big|_{T,P} = 0$$



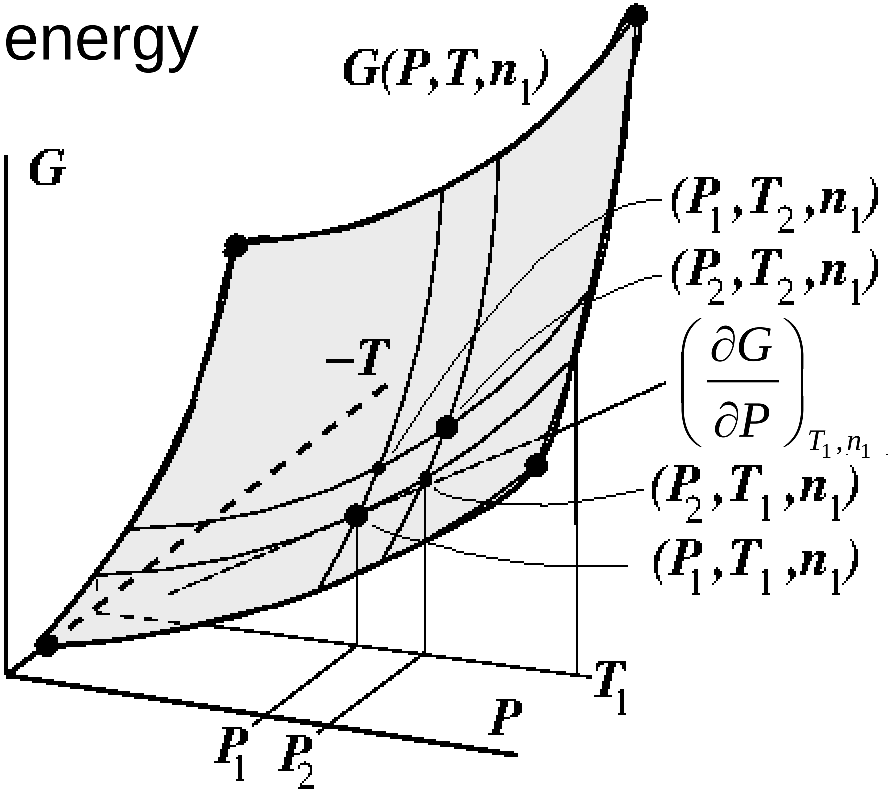
Total differential of a state function: ***G***

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$$

Gibbs free energy

$$dn = 0$$

(closed system)



V
follows
from the
equation
of state

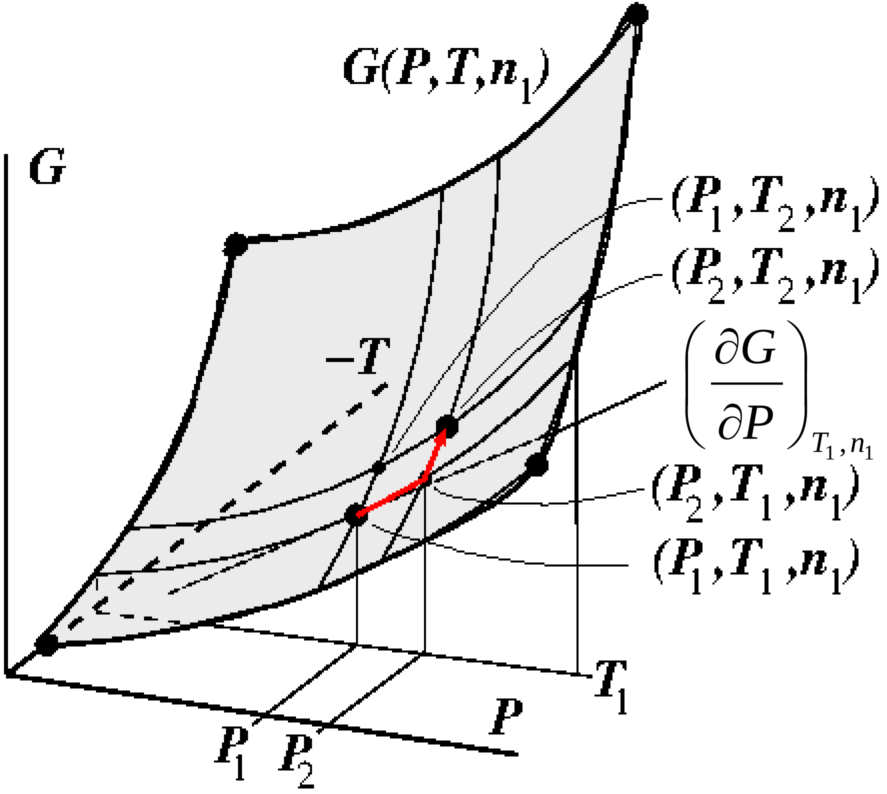
Process: (P_1,V_1,T_1,n_1) => (P_2,V_2,T_2,n_1)

Total differential of a state function: *G*

$$\boxed{\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T}$$

$$\boxed{dn = 0}$$

(closed system)



V

follows
from the
equation
of state

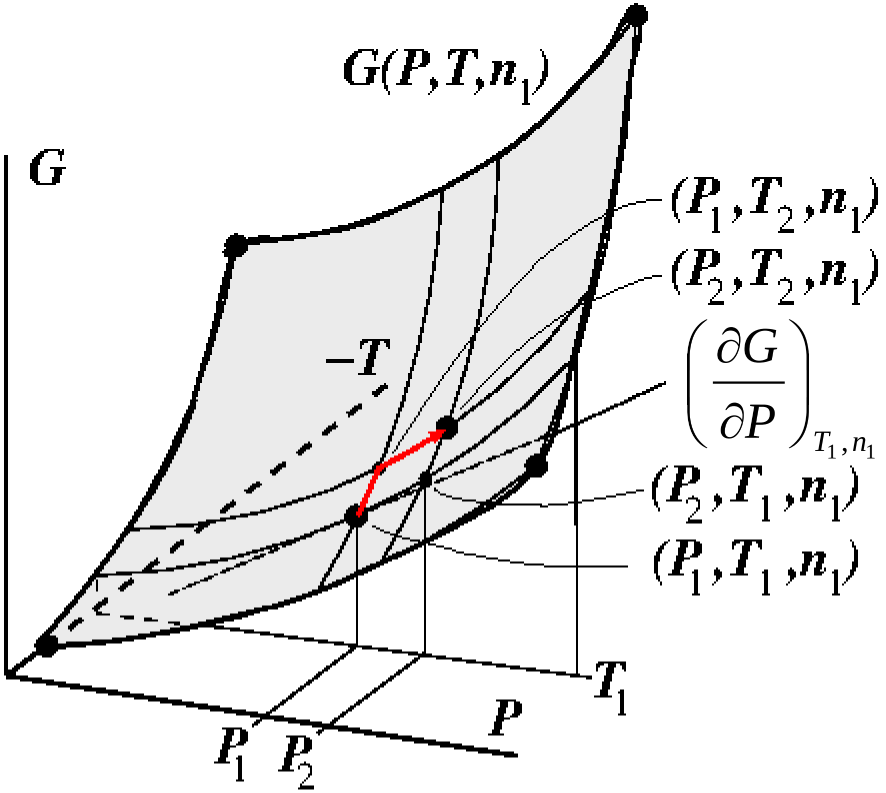
$$\Delta G(P_1,T_1 \rightarrow P_2,T_2)\Big|_n = \int_{P_1}^{P_2}\left(\frac{\partial G}{\partial P}\right)_{T_1,n}\mathrm{d}P + \int_{T_1}^{T_2}\left(\frac{\partial G}{\partial T}\right)_{P_2,n}\mathrm{d}T$$

Total differential of a state function: *G*

$$\boxed{\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T}$$

$$\boxed{dn = 0}$$

(closed system)



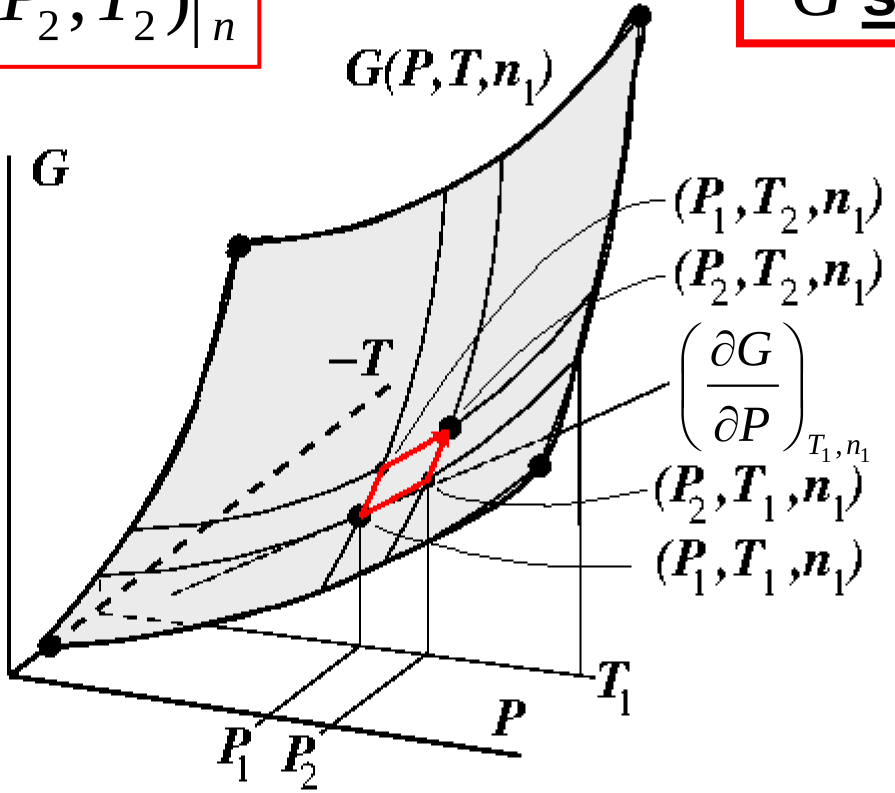
V
follows
from the
equation
of state

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

Total differential of a state function: *G*

$$\Delta G(P_1,T_1 \to P_2,T_2)\big|_n$$

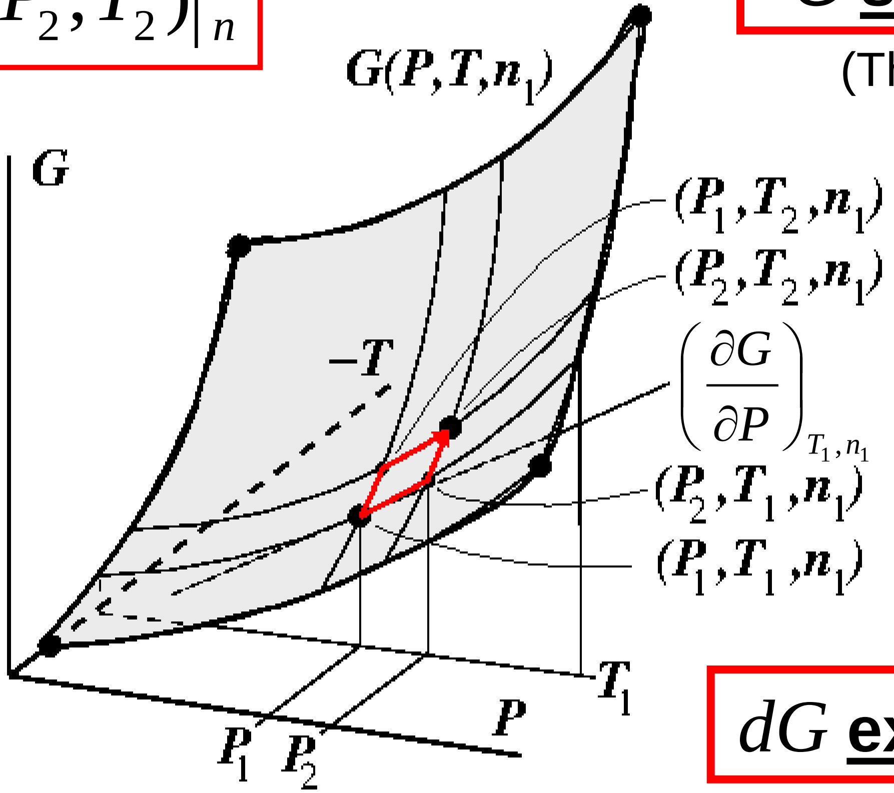
G **state function**



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

Total differential of a state function: *G*

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



G **state function**

(Thermodynamics)

(Mathematics)

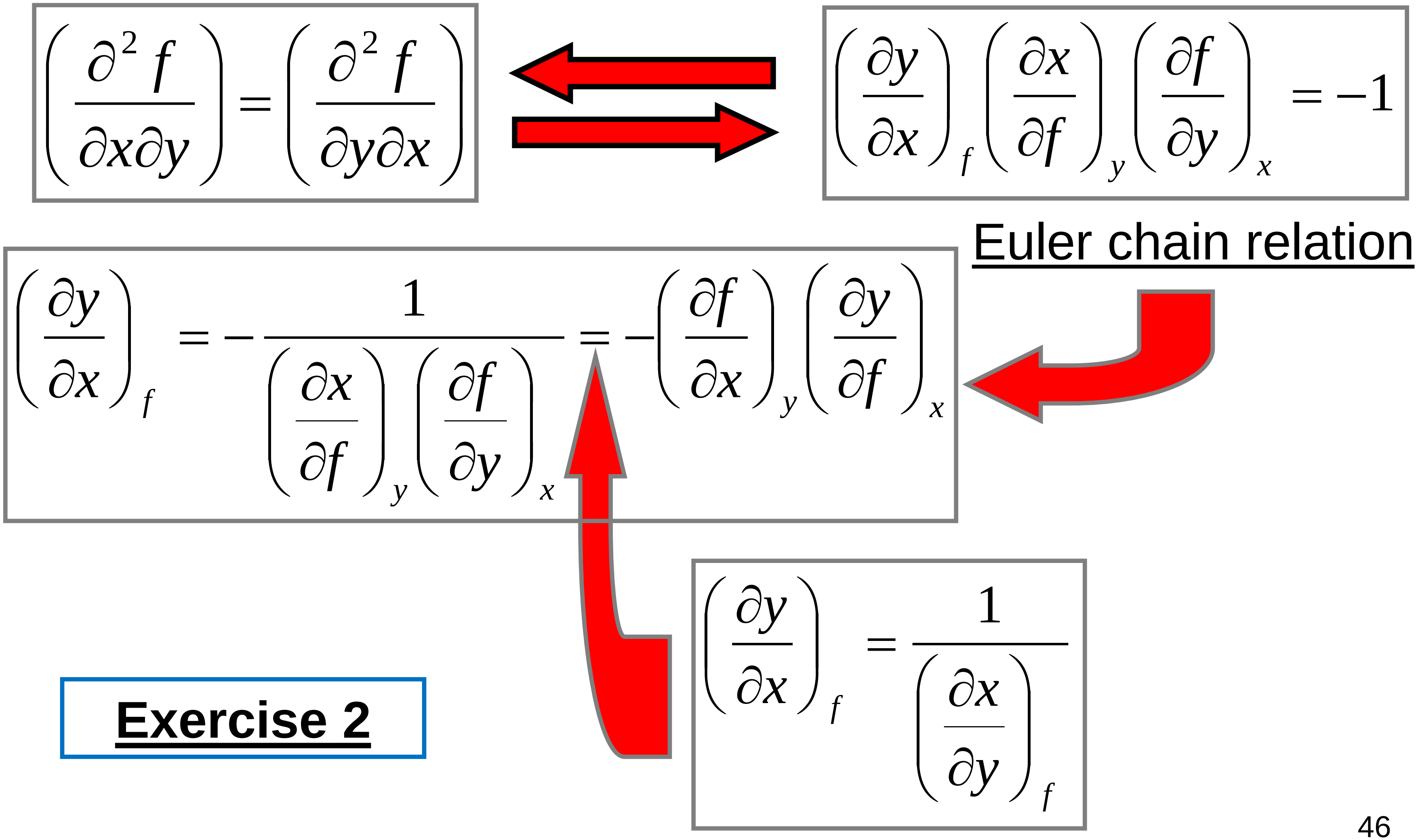
dG **exact differential**

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

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

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

(See Atkins p.105 (ed. 11 or 12); p.92 (ed.9))



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

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

Euler chain relation

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

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

Exercise 2

Exact differential of a state function: Maxwell relation

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

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$$

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

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

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

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

Maxwell relation

Exercise 3

Exact differential of a state function: Maxwell relations

$$\boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P}$$

Maxwell relations

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

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

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

James Clerk Maxwell
1831-1879

What is the use of these equations?

Exact differential of a state function: Maxwell relations

$$\boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P}$$

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

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

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

Exercise 4