Thermodynamics

Remedial Lecture 1

17 – 1 – 2022

Expectations

- Short repetition of theory, not replacing the course, not integrally repeating the course
- Exercises, level between tutor hour and tutorial
- Active participation
- Be prepared:
  - Study course material in the STUDY GUIDE & book (see website Thermo) *https://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html*
  - Bring formula sheet!!!

Course outline

- 5 sessions:
  - **1 Basics, (state) functions, ideal gas, internal energy, work, heat**
  - 2 Energy, Entropy
  - 3 Energy, chemical reactions
  - 4 Electrochemistry
  - 5 Colligative properties & statistical thermo

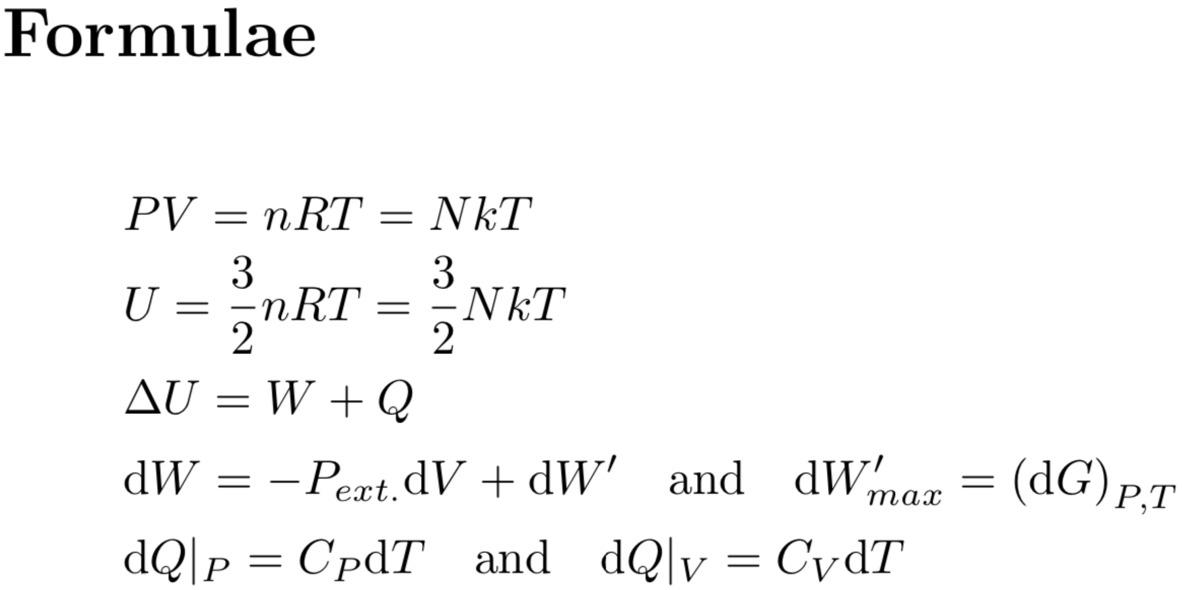
Course today

- Basics
  - Previous exams all contained 4 problems with each 4 subproblems with equal weight
  - (explanation of) formulas / quantities (always! 30 out of 160 points)

- Perfect monoatomic gas
  - Equations of state
  - Internal Energy, Work, Heat, Entropy, Enthalpy
  - relations

Basics include to study…….

- Study guide (page 4 – 7 & B1)
- Atkins (see study guide)
- Relevant formulas on formula sheet



Formulae

$$PV = nRT = NkT$$

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

$$\Delta U = W + Q$$

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

For reversible process

$$\mathrm{d}Q|_P = C_P\mathrm{d}T \quad \text{and} \quad \mathrm{d}Q|_V = C_V\mathrm{d}T$$

Basics include some definitions 1

- **State variables**

Macroscopic quantities (P, V, T, n, · · ·) that describe the thermodynamic state of a system.

- **Equation of state**

Relation between state variables that determines the possible states of the system in thermodynamic equilibrium, eg pV=nRT (Only for perfect gas)

- **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, eg H, G……, but also P,T,....

Basics include some definitions 2

- **Reversible process**

A process during which the system is in thermodynamic equilibrium at every moment

- **Irreversible process**

A process that is not necessarily reversible.

- **Isothermal process** $dT = 0$
- **Isobaric process** $dP = 0$
- **Isochoric process** $dV = 0$
- **Adiabatic process** $dQ = 0$
- **Isolated system** $dW = dQ = dn = 0$
- 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.

Exercise 1 often involves:

- the difference between “State function” (U, H, S etc) and “Equation of State” ($pV = nRT$)

- whether something is a “State function” or not

<u>State Function</u>: <u>not a State Function</u>:

mathematical operations
of the functions above:

$H + U$

pT

$S_{sys}T$

$\Delta U \Longleftarrow Q + W$?

$S_{\mathrm{sys}} \Longleftarrow S_{\mathrm{tot}} - S_{\mathrm{sur}}$?

Problem 1

a) Give a definition and/or *short* description of the following concepts

– perfect gas	Gas that complies with pV=nRT
– isobaric process	Process in which dP = 0
– activity	*Later*
– thermodynamic equilibrium constant	the value of the reaction quotient Q_t at equilibrium
– electromotive force	energy per unit electric charge

b) Indicate for each of the following quantities whether we are dealing with a state function; answer using only yes or no:

– the pressure P,	Yes
– the difference of internal energy and work $\Delta U - W$,	No (= Q)
– the product of temperature and entropy TS,	Yes
– the ratio of heat and temperature $\frac{Q}{T}$,	**No**
– the product of volume, pressure and temperature VPT.	Yes

Problem 1 (2017)

a) Give a definition and/or *short* description of the following concepts

- enthalpy
- isochoric process
- biological standard state conditions
- Raoult's law
- Boltzmann distribution

See Appendix B: Glossary and theory

b) Indicate for each of the following quantities whether we are dealing with a state function; answer using only yes or no:

- the volume V, **Yes**
- the difference of enthalpy and the product of pressure and volume $H - PV$, **= U Yes**
- the product of entropy and temperature ST, **Yes, S & T both are state functions**
- the product of entropy and the square of the temperature ST^2, **Yes**
- the product of charge and electric potential qE. **Yes**

c) Give the meaning of all symbols in the following formula as well as a description of its use in thermodynamic problems.

$$\Pi = \frac{n_B}{V} RT$$

To calculate the large molecular mass of substance B in a solution from a measured osmotic pressure due to a difference in concentration over a membrane.

First law of thermodynamics:

$$\Delta U = Q + W$$

- Q and W are NOT a state function, while U is a state function.

It is way more easy to work with state functions, that's why later on we are going to see whether we can discribe the heat as a state function

To keep things easy (for now), assume perfect gasses and only volume work

To calculate the heat:
$Q = \int C\, dT$ where C is the specific heat

We can distinguish several kinds of specific heat.
1. If we work at *constant volume* (isochoric process) we call the specific heat C_v
2. If we work at *constant pressure* (isobaric process) we call the specific heat C_p
3. The specific heat is given and constant (for a temperature interval)
4. The specific heat is given and a function of the temperature

ad. 1: If we have a mono-atomic perfect gas $C_v = 3/2nR$
ad. 2: If we have a mono-atomic perfect gas $C_p = 5/2nR$

Exercise 25

Consider a system consisting of 1 mol sodium, Na. In the table below a number of thermodynamic parameters is given.

	T_{fus}	$\Delta_{fus}H$	T_{vap}	$\Delta_{vap}H$
Na	371.0 K	2.601 kJ/mol	1156 K	98.01 kJ/mol

The heat capacity for all phases is given by (T is the temperature in K)

$$c_P(\mathrm{J/molK}) = A + BT + CT^2,$$

in which the parameters A, B and C, for temperatures $10\ K \leq T \leq 1500\ K$, in the three phases s(olid), l(iquid) and g(as) are given in the table below

Na	A(J/molK)	B(J/molK^2)	C(J/molK^3)
s	72.6	$-9.49 \cdot 10^{-3}$	$-731 \cdot 10^{-6}$
l	40.3	$-28.2 \cdot 10^{-3}$	$20.7 \cdot 10^{-6}$
g	20.8	$-0.277 \cdot 10^{-3}$	$-0.392 \cdot 10^{-6}$

a) At very high temperature the system behaves like a perfect gas.
What are the values of A, B and C in that case?

$\Delta U = Q + W$

To calculate the work we can use:

$$W = -\int p_{ext} dV$$

If we work isochoric: $dV = 0$ and there is no (volume-)work

If we work isobaric: p stays constant, get it out of the integral sign

$$W = -p_{ext} \int dV = -p_{ext} \Delta V$$

If we work reversible: $p_{ext} = p_{int}$ and since we consider a perfect gas $p=nRT/V$

$$W = -\int \frac{nRT}{V} dV$$

If we work reversible AND isothermic AND in a closed system:

$$W = -nRT \int \frac{1}{V} dV = -nRT ln(\frac{V_2}{V_1})$$

Exercise 1

We consider an isothermal reversible process.
We compress 2.0 mol of a perfect atomic gas isothermally and reversibly from 100 l to 25.0 l at a temperature of 50 °C.

a) Calculate the work W; Is this work done by the surroundings on the system or the other way around?

b) Calculate the heat Q; Is this heat supplied to the system or removed from it? Explain the sign of the result.

Since Q is not a state function, it could be beneficial to make the heat a state function.

Let’s define the enthalpy:

$$H = U + pV$$

which leads to:
$dH = dU + pdV + Vdp$
And with U $= Q + W = Q - pdV$

We could say that at constant pressure
$\mathrm{d}H = dU + pdV = Q - pdV + pdV = Q$

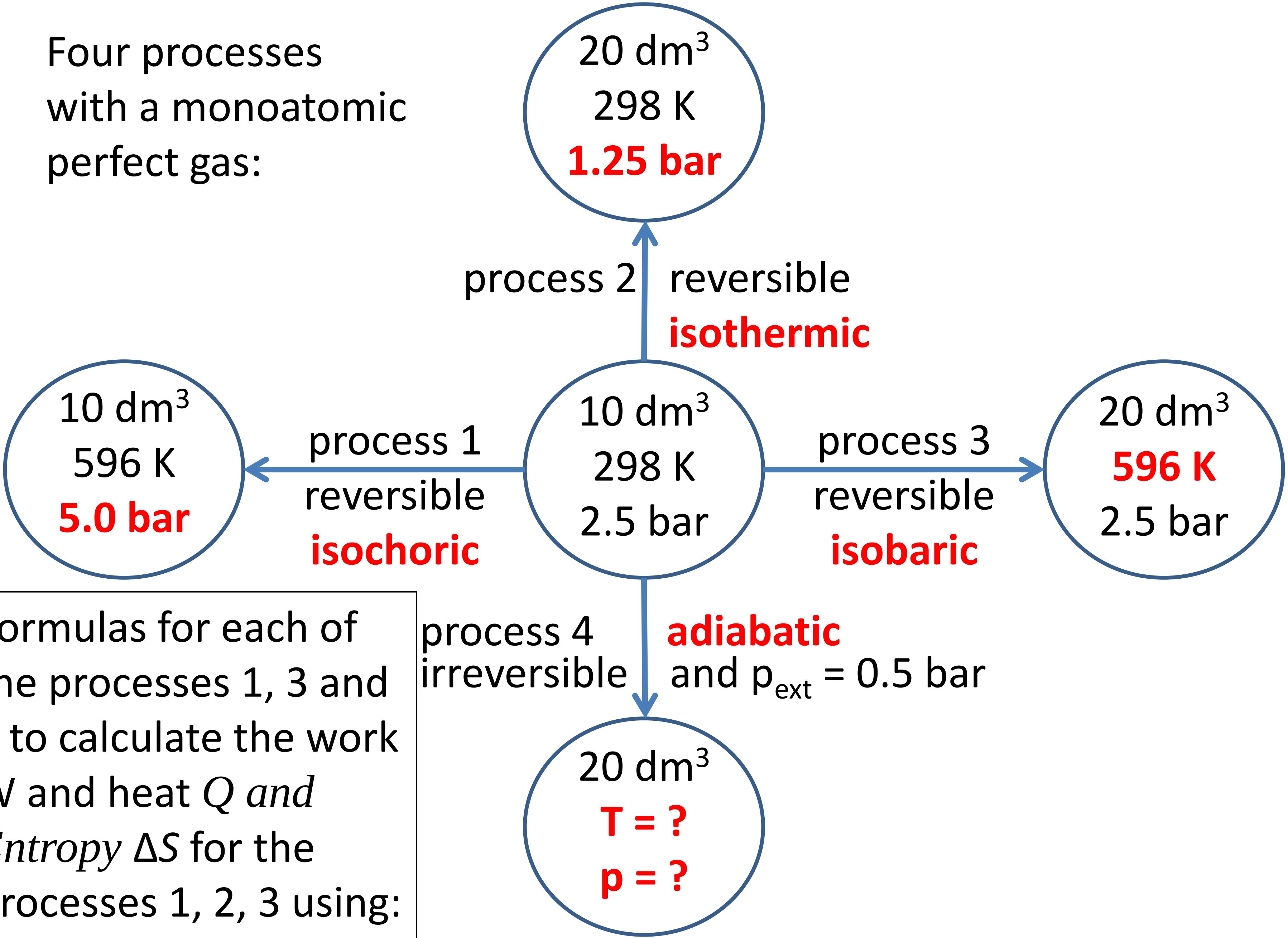
We now have created a state function for the heat! But only at constant pressure!

- The moral of this story
  - Basics are important to pass the exam
  - Wonder yourself with each step:
    - What am I doing (subject, question asked etc)
    - What is the meaning of symbols and constants used
  - Start practising with all material available:
    - Tutor hour
    - Tutorials *https://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html*

Perfect monoatomic gasses

- Learn to play with the formulas

Four processes
with a monoatomic
perfect gas:



$20\ \mathrm{dm^3}$
298 K
1.25 bar

process 2 reversible
isothermic

$10\ \mathrm{dm^3}$
596 K
5.0 bar

process 1
reversible
isochoric

$10\ \mathrm{dm^3}$
298 K
2.5 bar

process 3
reversible
isobaric

$20\ \mathrm{dm^3}$
596 K
2.5 bar

process 4
irreversible
adiabatic
and $p_{ext} = 0.5$ bar

$20\ \mathrm{dm^3}$
T = ?
p = ?

Formulas for each of the processes 1, 3 and 4 to calculate the work W and heat *Q and Entropy* Δ*S* for the processes 1, 2, 3 using:
$dS = dQ_{rev}/T$

a) Derive a formula to calculate the exerted work W for each of the four processes, using the formula:

$$W = -\int p\mathrm{d}V$$

Perfect gas law: $pV = n\mathrm{R}T; \quad p = \frac{n\mathrm{R}T}{V}$

No	kind of process	*W*	*Q*	*ΔU*
1	isochoric	**0**		
2	isothermic	$-n\mathrm{RT}\cdot\ln(V_f/V_i)$		
3	isobaric	$-p_{ext}\Delta V$		
4	adiabatic	$-p'_{ext}\Delta V$		

b) ΔU:
b) heat Q:

For a **monoatomic perfect gas** is defined: $U = 3/2 \cdot nRT$ so $\Delta U = 3/2 \cdot nR\Delta T$

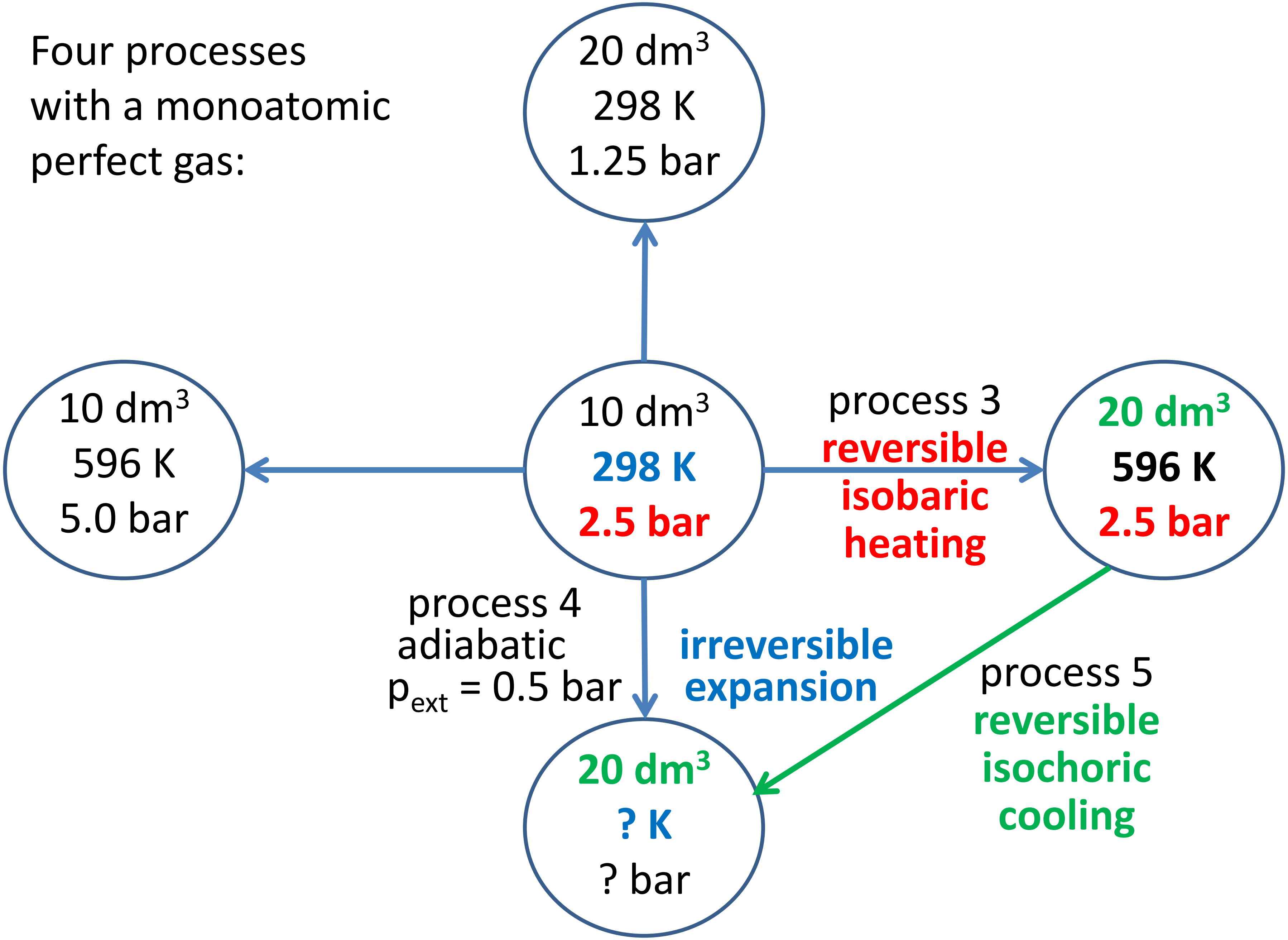
and: $C_V = 3/2 \cdot nR$

and: $C_p = 5/2 \cdot nR$

Nr	kind of process	W +	Q =	ΔU
1	isochoric	**0**	$3/2 \cdot nR\Delta T$ $\int C_V dT$ $C_V \Delta T$	$3/2 \cdot nR\Delta T$ $C_V \Delta T$
2	isothermic	$-nRT \cdot \ln(V_f/V_i)$	$+nRT \cdot \ln(V_f/V_i)$?	**0**
3	isobaric	$-p_{ext}\Delta V$ $-nR\Delta T$	$5/2 \cdot nR\Delta T$ $\int C_p dT$ $C_p \Delta T$	$5/2 \cdot nR\Delta T - nR\Delta T$ $C_p \Delta T - p\Delta V$ $3/2 \cdot nR\Delta T$
4	adiabatic	$-p_{ext}\Delta V$	**0**	$-p_{ext}\Delta V$

Nr	kind of process	Q	$\int dQ_{rev}/T$	$= \quad \Delta S$
1	isochoric	$\int C_v dT$	$\int (C_v/T)dT$	$C_v \cdot \ln(T_f/T_i)$
2	isothermic	$nRT \cdot \ln(V_f/V_i)$	$\longrightarrow$	$nR \cdot \ln(V_f/V_i)$
3	isobaric	$\int C_p dT$	$\int (C_p/T)dT$	$C_p \cdot \ln(T_f/T_i)$
4	adiabatic	e) irreversible process: you *have to* construct an alternative reversible path		

Four processes
with a monoatomic
perfect gas:



20 dm^3
298 K
1.25 bar

10 dm^3
596 K
5.0 bar

10 dm^3
298 K
2.5 bar

process 3
reversible
isobaric
heating

20 dm^3
596 K
2.5 bar

process 4
adiabatic
p_{ext} = 0.5 bar

irreversible
expansion

process 5
reversible
isochoric
cooling

20 dm^3
? K
? bar

Question 4 (from tutor hour)

A sample consisting of 1.00 mol of perfect gas atoms, initially at p_1= 1.00·10^5 Pa and T_1= 300 K, is heated reversibly to 400 K at constant volume. Calculate the final pressure, Δ*U*, *Q* and W

Question 4

$p_1/T_1 = p_2/T_2$; $p_2 = p_1 \cdot T_2/T_1 = 1.33 \cdot 10^5$ Pa

$\Delta U = 3/2 \cdot n\mathrm{R}\Delta T = 1247$ J

$W = -\int p\mathrm{d}V$ in which $\mathrm{d}V = 0$ so $W = 0$ J

$Q = \Delta U - W = 1247 - 0 = 1247$ J

2. 1.0 mole of helium of 25° C and p = p0 is reversibly and isothermically expanded until the pressure is 1.0 10^4 Pa. Given: Cv = 12.55 J K^{-1} mol^{-1}

a) Calculate the work done by the gas

b) Calculate the heat

3. 1.0 mole of helium of 25° C and $p = p0$ is adiabatically expanded until the pressure is 1.0 10^4 Pa.

a) Calculate the temperature after expansion
b) Calculate the volume after expansion
c) Calculate the work
d) Calculate the heat

1. 1.0 L hydrogen of 20° C and $p = p0$ is adiabatically compressed to a temperature of 80° C.

a) Calculate the volume after compression

b) Calculate the pressure after compression

c) Calculate the work, done on the gas

End for today!