

# Thermodynamics

Remedial Lecture 1

28 – 2 – 2024

# Course today

- Basics
  - Previous exam a lot of points were scored, or missed by being exact enough!
- Perfect, either monoatomic or not, gas
  - Equations of state
  - Internal Energy, Work, Heat, Entropy, Enthalpy
  - relations

# Basics include some definitions

- **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  $n$ .

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 describe the heat as a state function

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

To calculate the heat:

$$q = \int C dT \text{ where } C \text{ is the specific heat}$$

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  $C_p = 5/2nR$

$$\Delta U = q + w$$

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:

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

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:

$$dH = dU + pdV + Vdp$$

$$\text{And with } U = q + w = q - pdV$$

We could say that at **constant pressure**

$$dH = dU + pdV = dq - pdV + pdV = dq$$

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

For a perfect gas we know the gas law holds:

$$pV = nRT$$

For a mono-atomic perfect gas we also know:

$$C_v = 3/2 nR$$

and

$$C_p = 5/2 nR$$

This means that we can calculate  $\Delta U$  and/or  $\Delta H$  for a mono-atomic perfect gas quite easily:

$$\Delta U = 3/2 nR\Delta T \text{ and } \Delta H = 5/2 nR\Delta T$$

$\Delta U$  and  $\Delta H$  are (in a closed system) only dependent of  $\Delta T$ !

For a **non** mono-atomic perfect gas the latter still holds!

$$\Delta U = \int C_v dT \text{ (even if we are not at constant volume)}$$

$$\Delta H = \int C_p dT \text{ (even if we are not at constant pressure)}$$

For an adiabatic process it works slightly more difficult.

Adiabatic:  $q = 0$

If we can make it a reversible process, we can make a relation

$$dU = dq + dw = dw = -p_{ext}dV = -pdV$$

And  $dU = C_v dT$

If we have a perfect mono-atomic gas we can say:

$$\frac{3}{2} nRdT = -pdV = -\frac{nRT}{V}dV$$

Integrals in front of both sides:

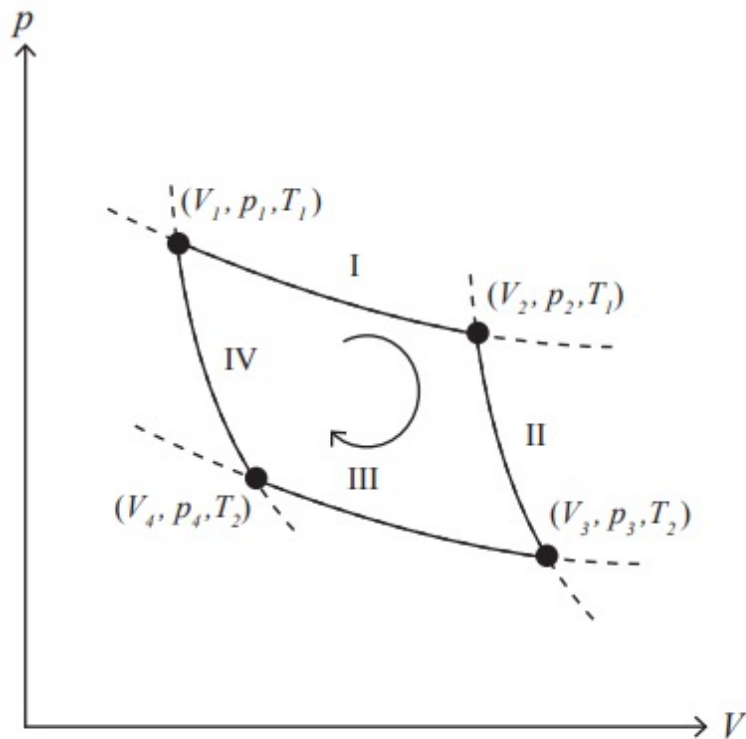
$$\int \frac{3}{2} nRdT = -\int \frac{nRT}{V}dV$$

And separating the variables:  $\frac{3}{2} \int \frac{1}{T} dT = -\int \frac{1}{V} dV$



1. (a) Explain what (i) an *isothermal* and (ii) an *adiabatic* process is. [2]

Consider the (schematic) diagram below that shows the Carnot cycle, consisting of four reversible steps: I, II, III and IV, in a  $PV$ -diagram.



- (b) (i) State for each of the steps I, II, III and IV whether they correspond to an isotherm or an adiabat? [2]
- (ii) For one mole of a perfect gas along step I, find  $w_{\text{rev}}$ ,  $q_{\text{rev}}$ ,  $\Delta U$  and  $\Delta S$  in terms of  $V_1$ ,  $V_2$ ,  $T_1$ , and  $R$ . [5]
- (iii) Given that the heat capacity for one mole of perfect gas is  $C_V = \frac{3}{2}R$ , show that for step II: [6]
- the change in entropy is  $\Delta S = 0$ ,
  - the final temperature  $T_2$  is given by  $T_2 = T_1 (V_2/V_3)^{2/3}$ ,
  - the change in internal energy is  $\Delta U = \frac{3}{2}R(T_2 - T_1)$ .

$$\text{b) ii) } w = - \int p_{ext} dV = - \int p dV = - \int \frac{nRT}{V} dV = -RT_1 \int \frac{1}{V} dV = -RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$q = \Delta U - w = -w$$

$$\Delta U = 0$$

$$\Delta S = \frac{q^{rev}}{T} = \frac{RT_1}{T_1} \ln\left(\frac{V_2}{V_1}\right)$$

$$\text{b) iii) adiabatic } dq = 0; \text{ reversible } dq^{rev} = 0; \Delta S = \frac{q^{rev}}{T} = 0$$

$$\frac{3}{2} \int \frac{1}{T} dT = - \int \frac{1}{V} dV \text{ makes: } \frac{3}{2} \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)$$

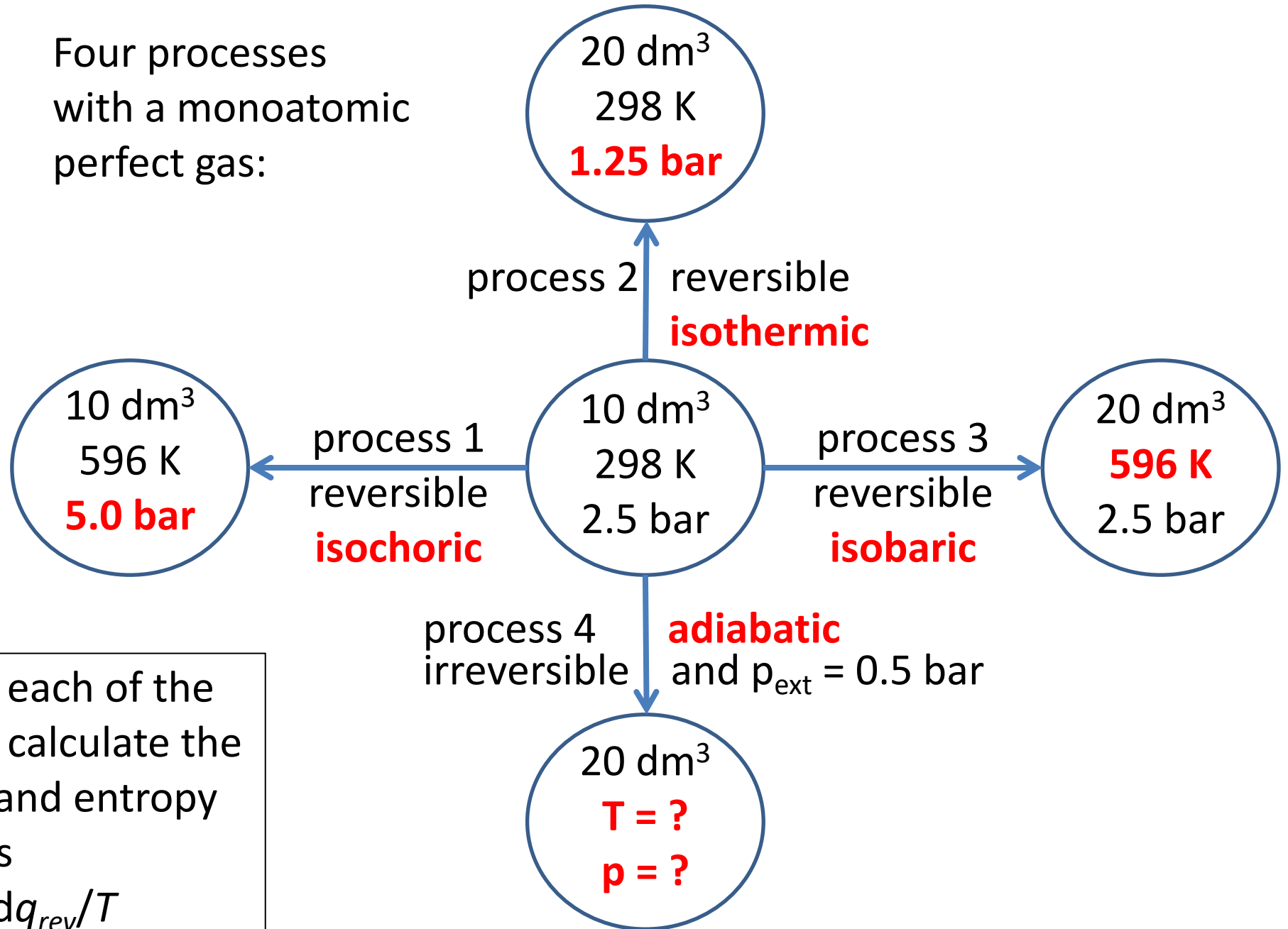
$$\text{Perfect mono atomic gas: } \Delta U = \frac{3}{2} R \Delta T$$

(c) The net work done by the gas during one cycle is given by  $w_{tot} = -nR \ln(V_2/V_1)(T_1 - T_2)$ .  
Explain whether the gas is doing work on the surroundings or not. [2]

$$V_2 > V_1 \text{ and } T_1 > T_2 \text{ so } \ln\left(\frac{V_2}{V_1}\right) \cdot (T_1 - T_2) > 0 \text{ and } w_{tot} < 0$$

So the system does work on the surroundings

Four processes  
with a monoatomic  
perfect gas:



Derive formulas for each of the processes 1, to 4 to calculate the work  $w$  and heat  $q$  and entropy  $\Delta S$  for the processes 1, 2, 3 using:  $dS = dq_{\text{rev}}/T$

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

$$w = - \int p dV \quad \text{Perfect gas law: } pV = nRT; \quad p = \frac{nRT}{V}$$

No	kind of process	$w$	$q$	$\Delta U$
1	isochoric	0		
2	isothermic	$-nRT \cdot \ln(V_f/V_i)$		
3	isobaric	$-p_{\text{ext}} \Delta V$		
4	adiabatic	$-p'_{\text{ext}} \Delta V$		

b) heat  $q$ :

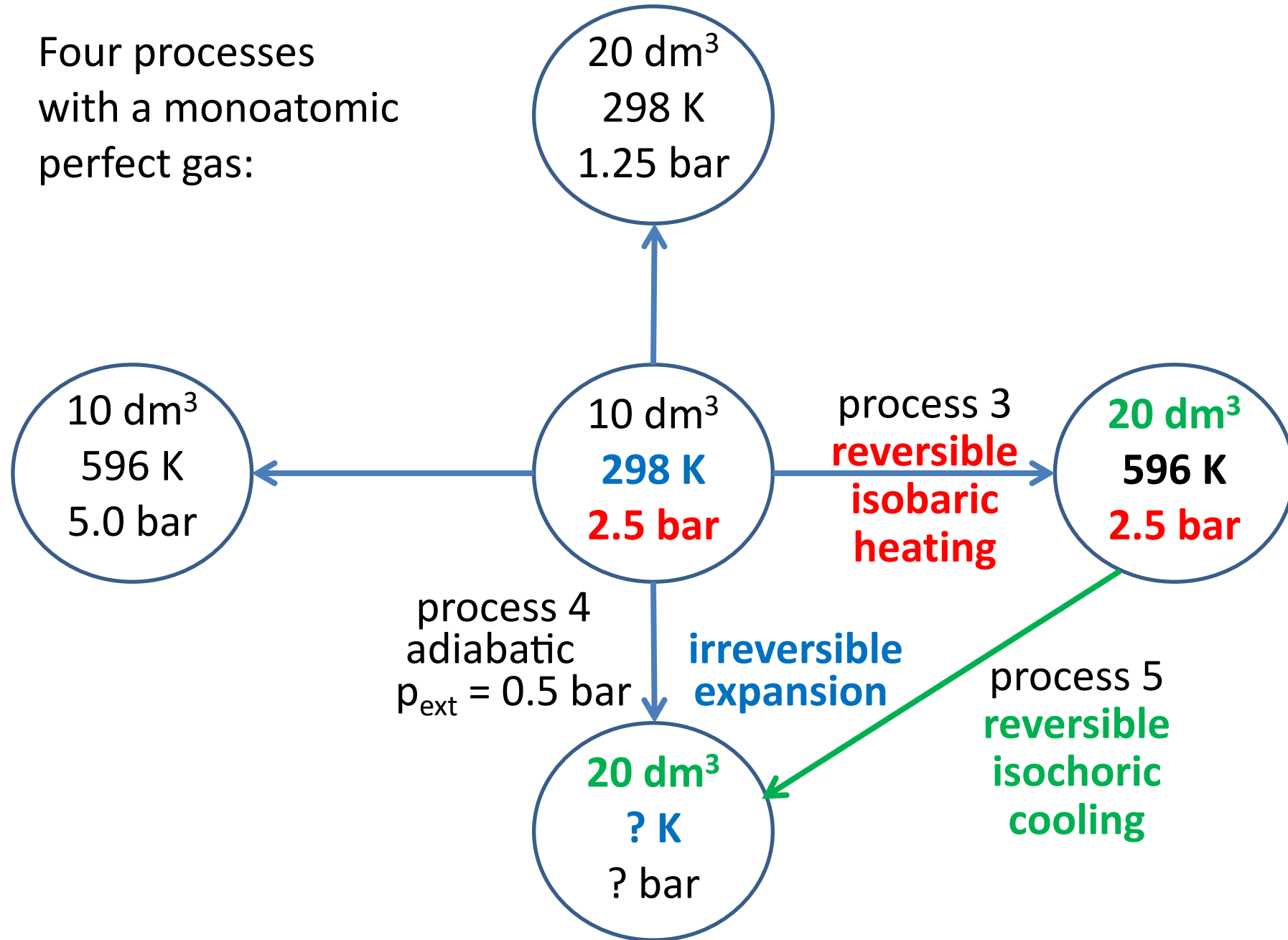
c)  $\Delta U$ :

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	$w$	$+ q =$	$\Delta U$
1	isochoric	0	<del><math>3/2 C_p nR \Delta T</math></del> $3/2 C_V nR \Delta T$	<del><math>3/2 C_p nR \Delta T</math></del> $3/2 C_V nR \Delta T$
2	isothermic	<del><math>-nRT \cdot \ln(V_f/V_i) + nRT \cdot \ln(V_f/V_i)</math></del>	<del><math>-nRT \cdot \ln(V_f/V_i) + nRT \cdot \ln(V_f/V_i)</math></del>	0
3	isobaric	<del><math>-p_{ext} \Delta V</math></del>	<del><math>5/2 C_p nR \Delta T</math></del> $5/2 C_p nR \Delta T$	<del><math>5/2 C_p nR \Delta T</math></del> $5/2 C_V nR \Delta T$
4	adiabatic	<del><math>-p_{ext} \Delta V</math></del>	0	<del><math>-p_{ext} \Delta V</math></del>

Nr	kind of process	$q$	$\int dq_{rev}/T$	= $\Delta S$
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	<b>e) irreversible process: you <i>have to</i> construct an alternative reversible path</b>		

Four processes  
with a monoatomic  
perfect gas:





## Phase transitions:

If a substance S is being heated (at constant pressure) from  $T_A$  (below melting point) to  $T_X$  (above boiling point), we can calculate the heat needed for this process with this formula:

$$\Delta H = \int_{T_A}^{T_{fus}} c_{p,solid} dT + \Delta_{fus} H + \int_{T_{fus}}^{T_{vap}} c_{p,liquid} dT + \Delta_{vap} H + \int_{T_{vap}}^{T_X} c_{p,gas} dT$$

$$\Delta S = \frac{q^{rev}}{T}$$

The cumulative entropy change in this case is:

$$\Delta S = \int_{T_A}^{T_{fus}} \frac{c_{p,solid}}{T} dT + \frac{\Delta_{fus} H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{c_{p,liquid}}{T} dT + \frac{\Delta_{vap} H}{T_{vap}} + \int_{T_{vap}}^{T_X} \frac{c_{p,gas}}{T} dT$$

2. (a) On cold nights, water spontaneously freezes to form ice. Explain how this is consistent with the Second Law of Thermodynamics, i.e., explain the role of  $\Delta S$  in determining the direction of spontaneous change. [2]
- (b) Given that for water  $C_p = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\Delta_{\text{fus}}H^\ominus = 6.00 \text{ kJ mol}^{-1}$  (note: fusion is melting), calculate the change in entropy for the process in which 1 mole water is cooled from  $10^\circ\text{C}$  to  $0^\circ\text{C}$  and then freezes to form ice at  $0^\circ\text{C}$  at  $p = p^\ominus$ . [4]

### Question 3

A sample consisting of 1.00 mol of perfect gas atoms, initially at  $p_1 = 1.00 \cdot 10^5$  Pa and  $T_1 = 300$  K, is heated reversibly to 400 K at constant volume. Calculate the final pressure,  $\Delta U$ ,  $q$  and  $w$ .

### Answers:

$$p_1/T_1 = p_2/T_2; \quad p_2 = p_1 \cdot T_2/T_1 = 1.33 \cdot 10^5 \text{ Pa}$$

$$\Delta U = 3/2 \cdot nR\Delta T = 1247 \text{ J}$$

$$w = -\int p dV \quad \text{in which } dV = 0 \quad \text{so } w = 0 \text{ J}$$

$$q = \Delta U - w = 1247 - 0 = 1247 \text{ J}$$

## Question 4

1.0 mole of helium of  $25^\circ\text{C}$  and  $p = p_0$  is reversibly and isothermally expanded until the pressure is  $1.0 \times 10^4\text{ Pa}$ .

Given:  $C_v = 12.55\text{ J K}^{-1}\text{ mol}^{-1}$

- a) Calculate the work done by the gas.
- b) Calculate the heat.

Answers:

a)  $w = 5706\text{ J}$

b)  $q = -5706\text{ J}$

## Question 5

1.0 mole of helium of  $25^\circ\text{C}$  and  $p = p_0$  is adiabatically expanded until the pressure is  $1.0 \times 10^4\text{ Pa}$ .

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

Answers:

a) 119 K

b) 97.5 L

c) 2238 J

d) 0 J

## Question 6

1.0 L hydrogen of 20°C and  $p = p_0$  is adiabatically compressed to a temperature of 80°C.

- Calculate the volume after compression.
- Calculate the pressure after compression.
- Calculate the work, done on the gas.

Answers:

- a) 0.631 L      b)  $1.91 \cdot 10^5$  Pa      c) 51.29 J

End for today!