

# *First law of thermodynamics*

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# First law of thermodynamics

The first law of thermodynamics claims that for a system of particles

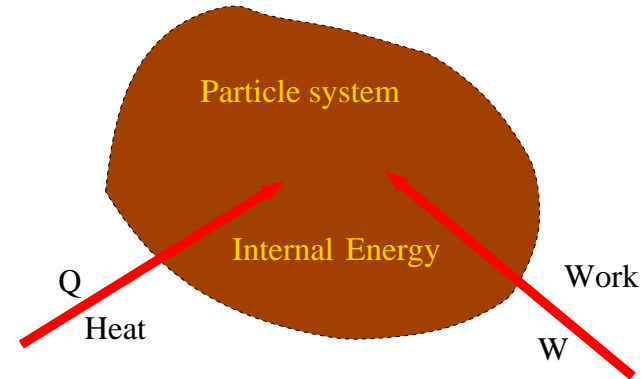
$$\Delta U_{int} = Q + W$$

where

$U_{int}$  is the internal energy of the system [J]

$Q$  is the heat supplied to the system [J]

$W$  is the work done on the system [J]



The first law of thermodynamics is a law of conservation of energy.

**Internal energy** is all the energy of a system that is associated with its microscopic components (atoms and molecules) when viewed from a reference frame at rest with respect to the center of mass of the system (Serway).

**Heat** is defined as a process of transferring energy across the boundary of a system because of a temperature difference between the system and its surroundings. It is also the amount of energy  $Q$  transferred by this process (Serway).

**Work** will be defined later

# Heat capacity

When the internal energy of a system is changed the temperature of the system is changed.

An exception to this statement is the case in which a system undergoes a change of state (also called a phase transition), this will be discussed later on.

If the change in internal energy only causes a temperature change, the heat capacity of the system is of great importance.

The **heat capacity**  $C$  of a particular sample of particles is defined as the amount of energy needed to raise the temperature of that sample by  $1\text{ }^{\circ}\text{C}$ . So if the energy  $\Delta U_{int}$  gives a raise in the temperature of  $\Delta T$ ,  $C$  is given as

$$C = \frac{\Delta U_{int}}{\Delta T}$$

The **specific heat capacity** is given as

$$c = \frac{\Delta U_{int}}{M \Delta T}$$

where  $M$  is the mass. For specific heat capacity, often just named specific heat, values can be found on the internet.

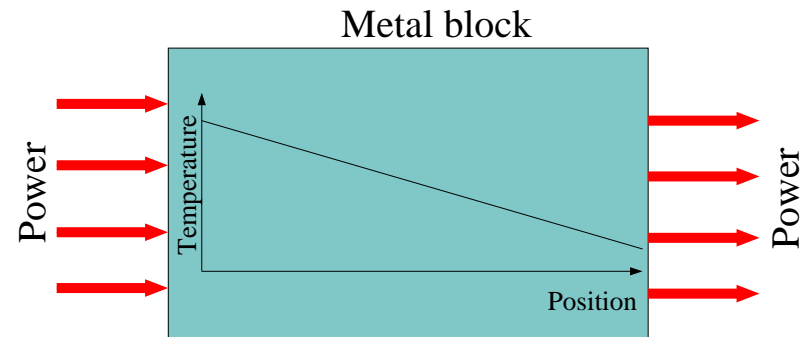
# First law, conduction

If we have a system where the only change in internal energy can be observed by a temperature change the first law gives

$$\Delta U_{int} = Mc\Delta T = Q + W$$

The heat  $Q$  can be described by **thermal conduction**, **radiation** or **convection**.

**Thermal conduction** is a process where at an atomic scale exchange of kinetic energy between microscopic particles, molecules, atoms, and free electrons, in which less energetic particles gain energy in collisions with more energetic particles takes place. Conduction occurs only if there is a difference in temperature between two parts of the conducting medium. It is found that **power**  $\mathcal{P}$ , defined as



$$\mathcal{P}(t) = \frac{dQ(t)}{dt},$$

is proportional to the cross-sectional area  $A$  and the temperature difference  $dT$  and inverse proportional to the thickness  $dx$

$$\mathcal{P}_{conduction} = kA \left| \frac{dT}{dx} \right|$$

where  $k$  is called thermal conductivity of the material and values may be found on the internet.

# *First law, radiation*

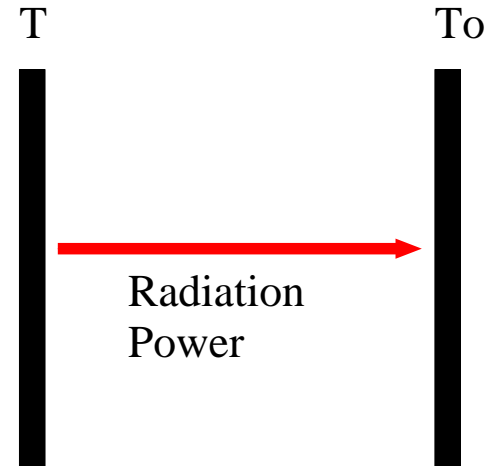
**Radiation** is energy transfer in the form of electromagnetic waves produced by thermal vibrations of the molecules.

The power is transferred between two surfaces given by

$$\mathcal{P}_{radiation} = A\sigma(T^4 - T_o^4)$$

where  $A$  is the area,  $\sigma$  is a value that depends e.g. of the color of the surfaces and  $T$  respective  $T_o$  are the temperatures of the surfaces.

Radiation normally only plays an important role if the temperatures are high for example in a combustion chamber.



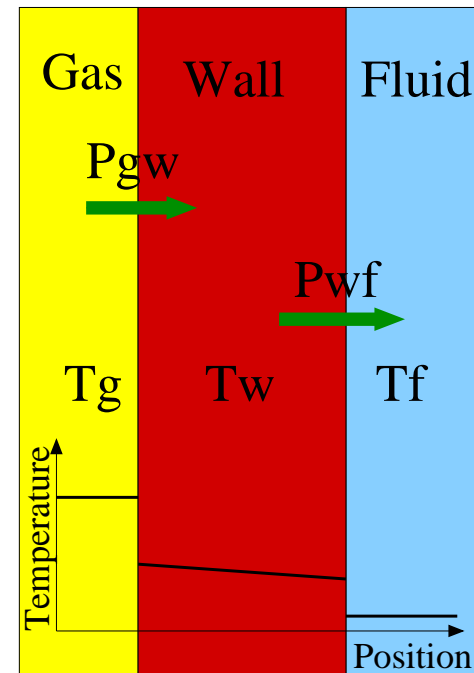
# First law, convection

**Convection** is a mechanism where energy is transferred from a wall to a moving fluid/gas. It could be from a radiator to the air or from the water in the radiator to the radiator metal; the first is called natural convection the latter is called forced convection. The transfer is a combination of motion of particles and conduction. The power is given by

$$\mathcal{P}_{convection} = A\alpha(T - T_o)$$

where  $A$  is the area, the  $T$ 's are mentioned in radiation and  $\alpha$  is the heat transfer coefficient.

The heat transfer coefficients  $\alpha$  play an important role, but unfortunately, they can be problematic to find, because they depend on very many factors such as the form of the wall (flat, curved etc.), the state of the fluid (density, viscosity, specific heat, conductivity, temperature, pressure etc.), the velocity of the fluid (laminar, turbulent), phase shifts along the wall. To find the heat transfer coefficients consult textbooks like (Chapman84)



# Energy and power

Until now the terms energy and power have been used. The relation is

$$\mathcal{P}(t) = \frac{dQ(t)}{dt} \quad Q(t) = \int_0^t \mathcal{P}(\tau) d\tau + Q(t=0)$$

where the unit of energy  $Q$  is Joule and power  $\mathcal{P}$  is Joule/sec = Watt.

The first law is for a system of particles where the only change in internal energy can be observed by a temperature change

$$\begin{aligned} \Delta U_{int} &= Mc\Delta T = Q + W \Rightarrow \\ \frac{dU_{int}}{dt} &= \frac{d(Mc\Delta T)}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} \end{aligned}$$

Assuming constant mass and specific heat capacity we find

$$Mc \frac{d(\Delta T)}{dt} = \mathcal{P}_{convection} + \mathcal{P}_{radiation} + \mathcal{P}_{conduction} + \frac{dW}{dt}$$

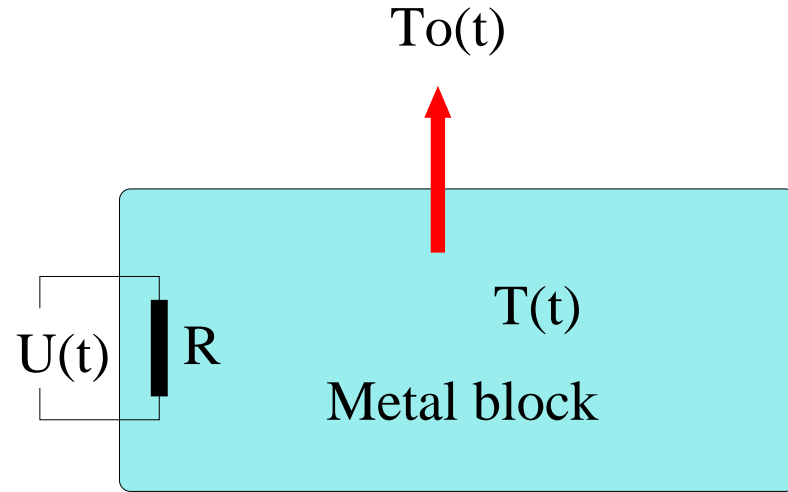
# Example using first law

## Heating of metal block

We can use the first law to find a model

$$Mc \frac{dT}{dt} = \mathcal{P}_{convection} + \frac{dW}{dt}$$

where we assume no radiation from the block and no conduction.



The term  $\frac{dW}{dt}$  with the unit Watt is the electrical power from the resistor and this is given as  $\mathcal{P}_{elec} = \frac{U^2}{R}$ , where  $R$  is the resistance. The term  $\mathcal{P}_{convection}$  is the heat loss from the block to the ambient.

The differential equation describing the system is

$$Mc \frac{dT(t)}{dt} = \alpha A (T(t) - T_o(t)) + \frac{U^2(t)}{R}$$

where it can be seen which terms are considered to vary in time and which are constants.

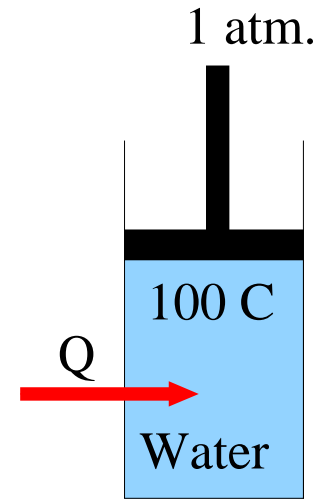
The differential equation is non-linear and if the aim is to find a transfer function the equation must be linearised.



# Latent heat

Until now we have assumed that the internal energy of the system of particles can be observed by just measuring the temperature.

But assume that the system consist of a mixture of water and steam at  $100\text{ }^{\circ}\text{C}$ , kept at a constant pressure of 1 atm. The particles can be in a cylinder with a weightless piston, then the pressure inside the cylinder will be the same as the ambient pressure. If we add more heat  $Q$  to the system the internal energy  $U_{int}$  will raise, but the temperature will stay at  $100\text{ }^{\circ}\text{C}$ , instead the internal energy raise by changing some water to steam. In this case the temperature can not be used to observe the energy.



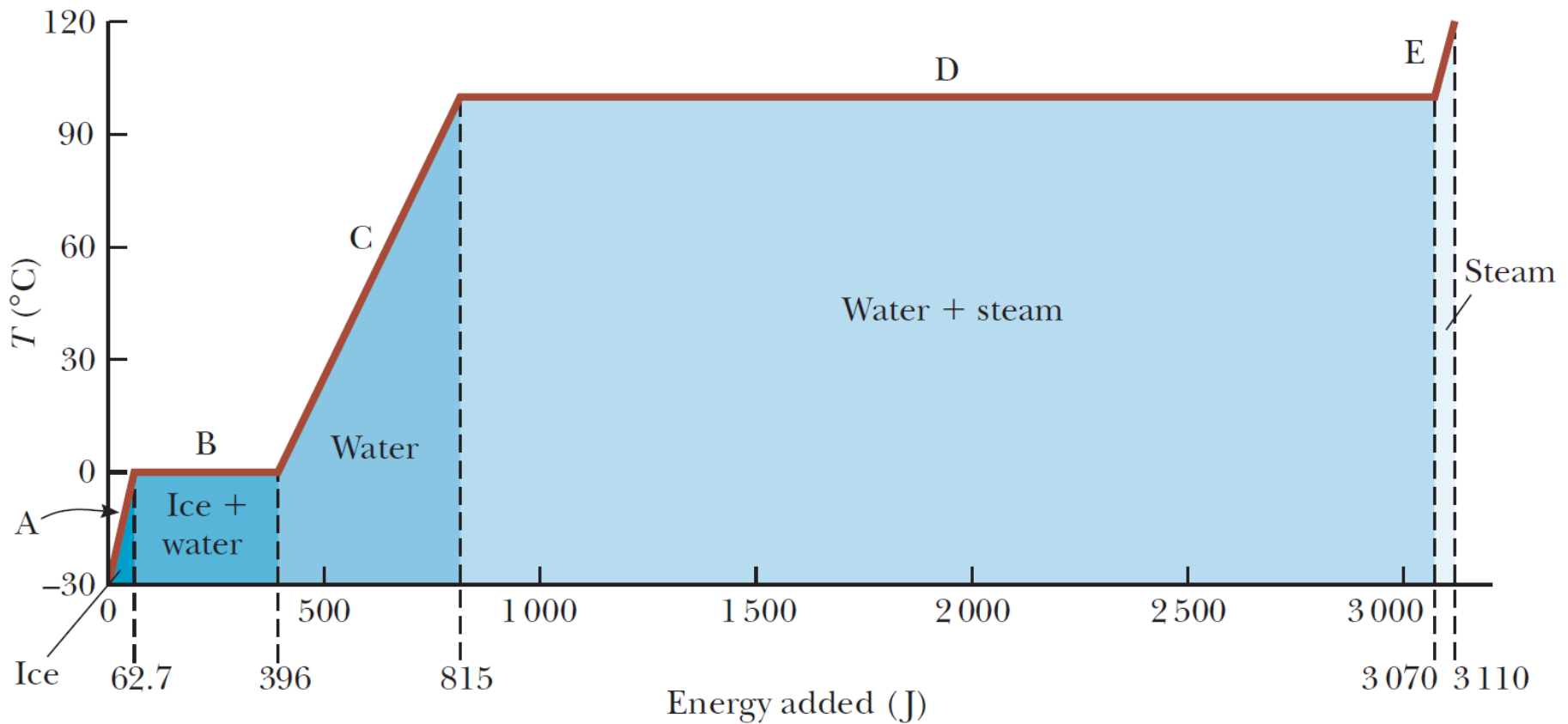
**Latent heat** is a useful term to describe this phase change. The latent heat (literally, the 'hidden' heat) is the energy that is needed to phase shift 1 kg from one phase to another phase; it is assumed that the material is in a saturated state. Latent heat  $L$  is defined by

$$L = \frac{Q}{\Delta M}$$

where  $\Delta M$  is mass that changes phase.

# Latent heat

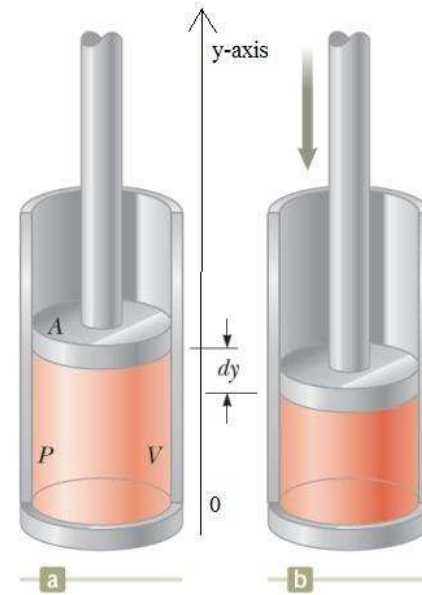
In the figure (Serway) 1 gram of ice is added energy until the ice has been converted to 120 deg. steam; the pressure is 1 atm.



# Work

**Work** in thermodynamic processes is defined using the definition from mechanical systems where it is defined as force multiplied with displacement.

In the figure a force  $F$  gives rise to a displacement  $dy$  so that the work done on the cylinder system from a to b is  $dW = -Fdy$ . (The negative sign is because  $dy$  is negative).



The force is given by the pressure  $P$  multiplied with the cross-sectional area  $A$  so  $dW = -Fdy = -PA dy$ . Because  $A dy$  is the change in volume of the gas  $dV$  the work on the gas is

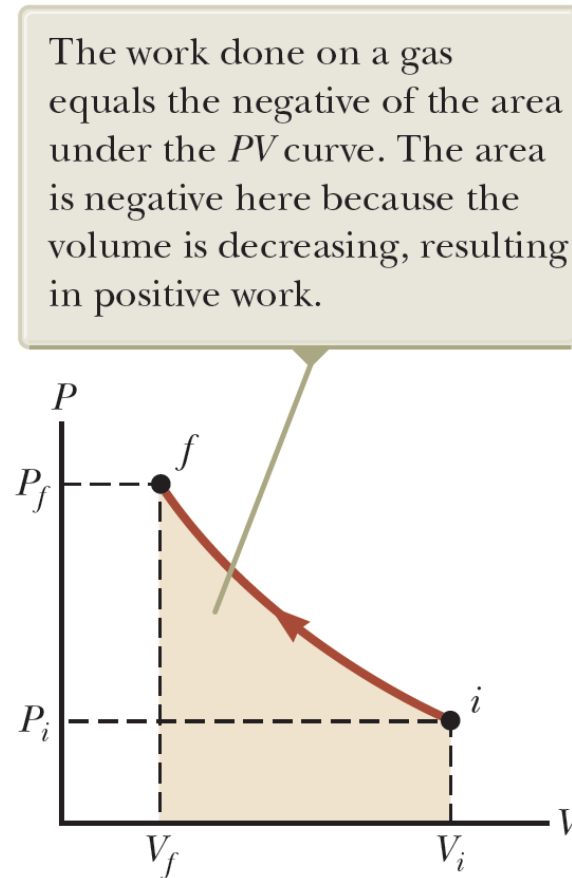
$$dW = -PdV$$

# Work

The total work done on the gas as its volume changes from  $V_i$  to  $V_f$  is given by the integral

$$W = - \int_{V_i}^{V_f} P dV$$

In a pressure – volume (PV) diagram as shown in the figure the work is the negative area under the curve.



# Work

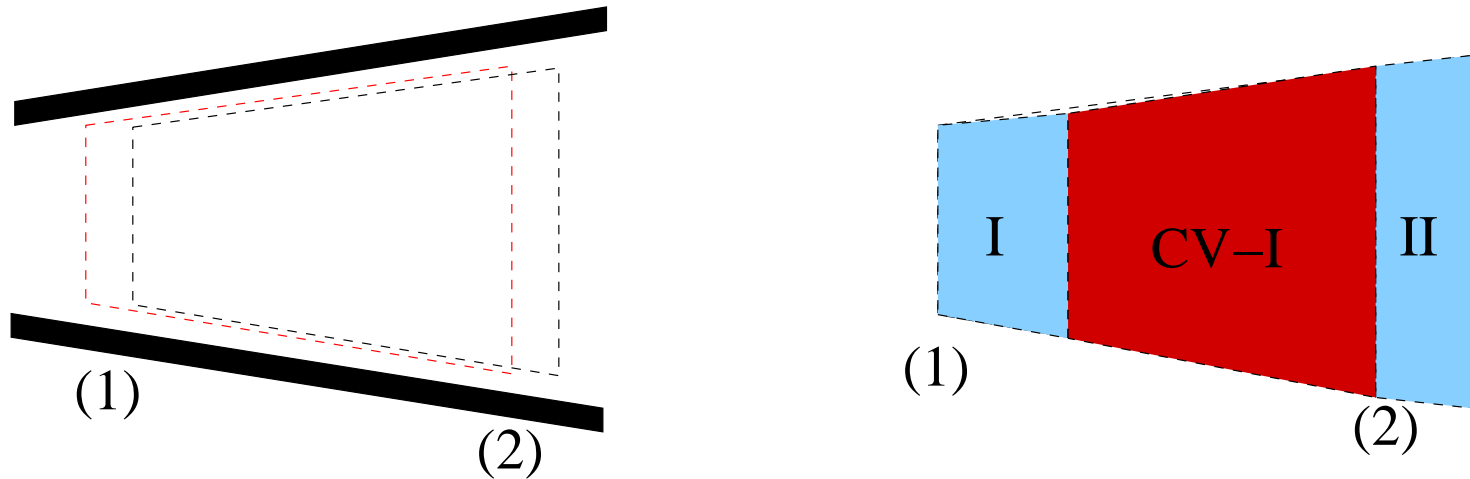
For an ideal gas with constant temperature we have that  $PV = nRT$  is constant; it can be proved that the work associated with **isothermal expansion** is given by

$$W = nRT \ln\left(\frac{V_i}{V_f}\right)$$

As a second property for an ideal gas under **adiabatic (isolated) expansion**, the curve in the PV diagram is given as  $PV^\gamma = \text{constant}$ , where  $\gamma$  depends on the ideal gas and  $\gamma > 1$ . These results will play a role in a later proof.

# Control volume

Next we will go from considering a **system of particles** and instead focus on a **control volume** called CV. A simple version of relating the system concept to the control volume concept can be obtained from the one-dimensional flow through a fixed control volume as shown in the figure.

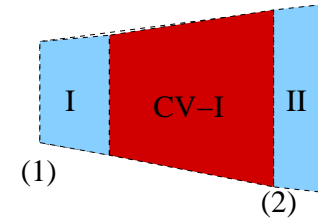


- Fixed CV surface and particle system boundary at time  $t$
- Particle system boundary at time  $t + \Delta t$

The CV is fixed in the tube and it is marked by (1) and (2). The particle system is marked by the dashed line. We see that at time  $t$  the system and the CV coincide. At time  $t + \Delta t$  the system has moved and now occupies section  $(CV - I) + II$ .

# Control volume

We can now look at a certain property of the system described by the general parameter  $B$ , where  $B$  can be mass or energy. Then at time  $t$  we have  $B_{sys}(t) = B_{CV}(t)$  At time  $t + \Delta t$  the system is



$$B_{sys}(t + \Delta t) = B_{CV}(t + \Delta t) - B_I(t + \Delta t) + B_{II}(t + \Delta t)$$

now if  $B_{sys}(t)$  is subtracted and we divide by  $\Delta t$

$$\frac{B_{sys}(t + \Delta t) - B_{sys}(t)}{\Delta t} = \frac{B_{CV}(t + \Delta t) - B_I(t + \Delta t) + B_{II}(t + \Delta t) - B_{sys}(t)}{\Delta t}$$

Letting  $\Delta t \rightarrow 0$

$$\frac{d(B_{sys}(t))}{dt} = \frac{d(B_{CV}(t))}{dt} - \lim_{\Delta t \rightarrow 0} \frac{B_I(t + \Delta t)}{\Delta t} + \lim_{\Delta t \rightarrow 0} \frac{B_{II}(t + \Delta t)}{\Delta t}$$

The two terms

$$\lim_{\Delta t \rightarrow 0} \frac{B_I(t + \Delta t)}{\Delta t} = b_{in}(t) \quad \text{and} \quad \lim_{\Delta t \rightarrow 0} \frac{B_{II}(t + \Delta t)}{\Delta t} = b_{out}(t)$$

$$\frac{d(B_{sys}(t))}{dt} = \frac{d(B_{CV}(t))}{dt} - b_{in}(t) + b_{out}(t)$$

# Mass balance

We can for instance consider the mass of system of particles  $M_{sys}$  vs the mass a control volume  $M_{CV}$ . Conservation of mass implies

$$\begin{aligned}\frac{d(M_{sys}(t))}{dt} &= 0 = \frac{d(M_{CV}(t))}{dt} - m_{in}(t) + m_{out}(t) \\ \frac{dM_{CV}(t)}{dt} &= m_{in}(t) - m_{out}(t)\end{aligned}$$

Then the **mass balance** is

$$\boxed{\frac{dM_{CV}(t)}{dt} = m_{in}(t) - m_{out}(t)}$$

where  $M_{CV}$  is the mass in the CV,  $m_{in}$  is the mass flow going into the CV and  $m_{out}$  is the mass flow going out of the CV. The unit of mass flow is kg/sec.



# Energy balance

If  $B$  in the general B-equation is energy we can define energy flow associated with the streams in and out as  $\mathcal{P}_{in,flow}$  and  $\mathcal{P}_{out,flow}$

$$\frac{d(U_{sys}(t))}{dt} = \frac{d(U_{CV}(t))}{dt} - \mathcal{P}_{in,flow}(t) + \mathcal{P}_{out,flow}(t)$$

The left side of the equation is given by the first law

$$\frac{dQ}{dt} + \frac{dW}{dt} = \frac{d(U_{CV}(t))}{dt} - \mathcal{P}_{in,flow}(t) + \mathcal{P}_{out,flow}(t)$$

The first term is the power to the system from conduction, radiation and convection, we can denote this as  $P_{ext}$ .

$$\frac{d(U_{CV}(t))}{dt} = \mathcal{P}_{ext}(t) + \mathcal{P}_{in,flow}(t) - \mathcal{P}_{out,flow}(t) + \frac{dW(t)}{dt}$$

The internal energy in the CV is given as the specific internal energy  $u$  multiplied with the mass ( $U_{CV} = M_{CV}u_{CV}$ ). The power in the flow are given as the flow multiplied by the internal energy ( $\mathcal{P}_{in,flow} = m_{in}u_{in}$ ,  $\mathcal{P}_{out,flow} = m_{out}u_{out}$ )

$$\frac{d(M_{CV}u_{CV}(t))}{dt} = \mathcal{P}_{ext}(t) + m_{in}u_{in}(t) - m_{out}u_{out}(t) + \frac{dW(t)}{dt}$$

# Energy balance, work

The work term  $dW$  is the nett work done on the system and associated to the inflow and outflow,  $dW = dW_{in} - dW_{out}$ . Remembering that the work is force multiplied by displacement

$$dW = dW_{in} - dW_{out} = F_{in}dy_{in} - F_{out}dy_{out}$$

The force equals pressure multiplied with cross-sectional area  $A$ . The displacement is velocity multiplied with time

$$dW = F_{in}dy_{in} - F_{out}dy_{out} = P_{in}A_{in}v_{in}dt - P_{out}A_{out}v_{out}dt$$

The velocity perpendicular to  $A$  is given by  $v = m \frac{1}{\rho} \frac{1}{A}$ , where  $\rho$  is density.

$$dW = P_{in}A_{in}v_{in}dt - P_{out}A_{out}v_{out}dt = P_{in} \frac{1}{\rho_{in}} m_{in} dt - P_{out} \frac{1}{\rho_{out}} m_{out} dt$$

giving

$$\frac{dW}{dt} = P_{in} \frac{1}{\rho_{in}} m_{in} - P_{out} \frac{1}{\rho_{out}} m_{out}$$

Putting this in the equation on the previous slide

$$\frac{d(M_{CV}(t)u_{CV}(t))}{dt} = \mathcal{P}_{ext}(t) + m_{in}(t)u_{in}(t) - m_{out}(t)u_{out}(t) + \frac{P_{in}(t)}{\rho_{in}(t)} m_{in}(t) - \frac{P_{out}(t)}{\rho_{out}(t)} m_{out}(t)$$

# General energy balance

Defining **specific enthalpy**  $h$  as  $h = u + \frac{P}{\rho}$  gives

$$\frac{d(M_{CV}(t)u_{CV}(t))}{dt} = \mathcal{P}_{ext}(t) + m_{in}(t)h_{in}(t) - m_{out}(t)h_{out}(t)$$

In some textbooks this is called the energy balance.

If the term  $\frac{d(M_{CV}\frac{P}{\rho})}{dt} = \frac{d(PV_{CV})}{dt}$  is added ( $V_{CV}$  is volume)

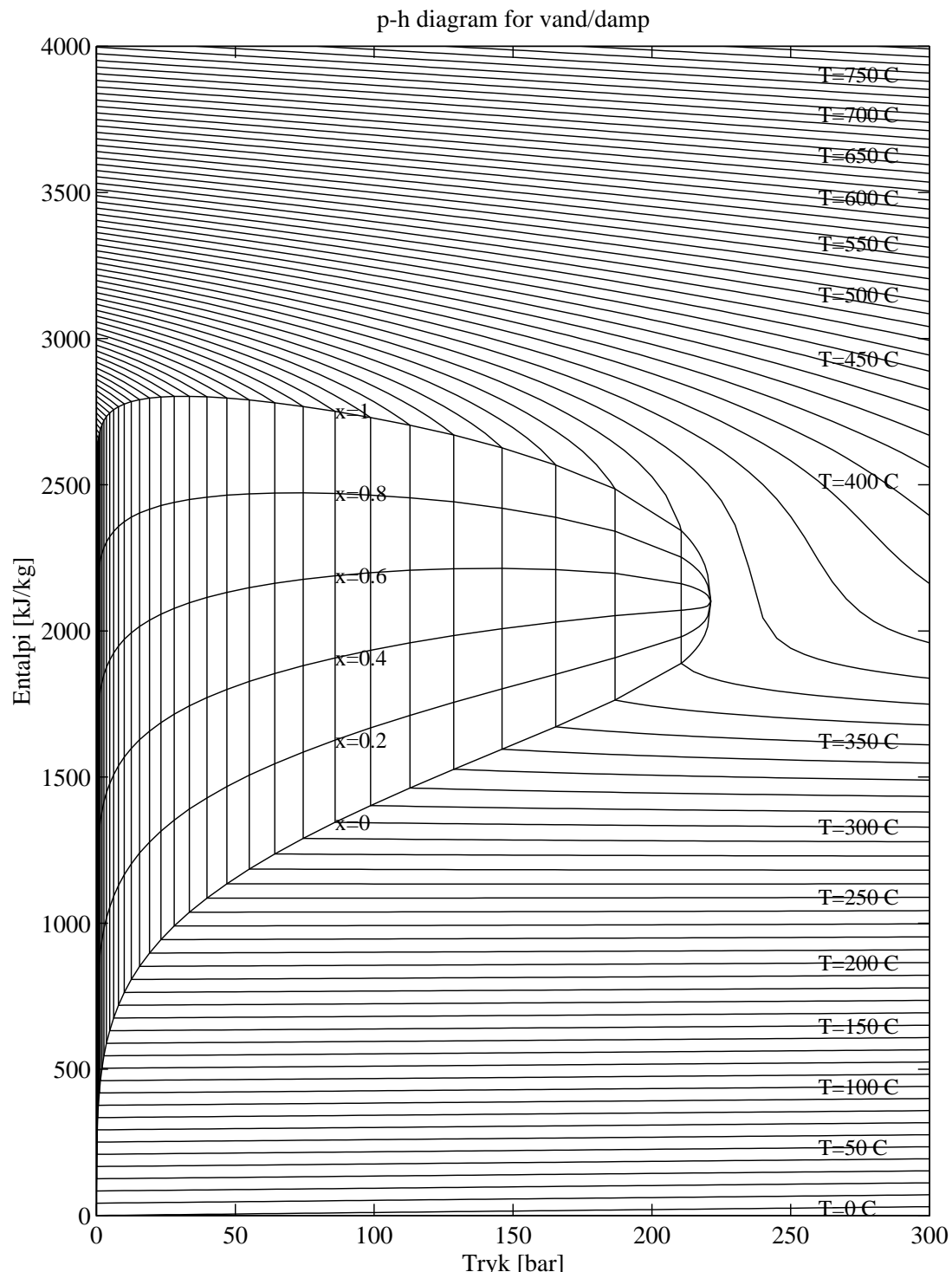
$$\frac{d(M_{CV}(t)h_{CV}(t))}{dt} = \mathcal{P}_{ext}(t) + m_{in}(t)h_{in}(t) - m_{out}(t)h_{out}(t) + V_{CV}\frac{d(P(t))}{dt}$$

and the term  $V_{CV}\frac{d(P(t))}{dt}$  is negligible we find the **energy balance**

$\frac{d(M_{CV}(t)h_{CV}(t))}{dt} = \mathcal{P}_{ext}(t) + m_{in}(t)h_{in}(t) - m_{out}(t)h_{out}(t)$
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The unit of specific enthalpy is Joule/kg.

# Enthalpy



# One phase energy balance

The specific heat for constant pressure is

$$c_p = \left. \frac{\partial h}{\partial T} \right|_{P=\text{constant}}$$

Because  $c_p$  in certain temperature intervals is nearly constant, (this is the case where only one phase exist) a good approximation for the enthalpy is

$$h \approx c_p \cdot T$$

This mean that for a matter that do not change phase the **One phase energy balance** is

$$\boxed{\frac{d(c_{CV} M_{CV}(t) T_{CV}(t))}{dt} = \mathcal{P}_{ext}(t) + c m_{in}(t) T_{in}(t) - c m_{out}(t) T_{out}(t)}$$

Normally the specific heat  $c$  is assumed to be constant