



A refresher in engineering thermodynamics

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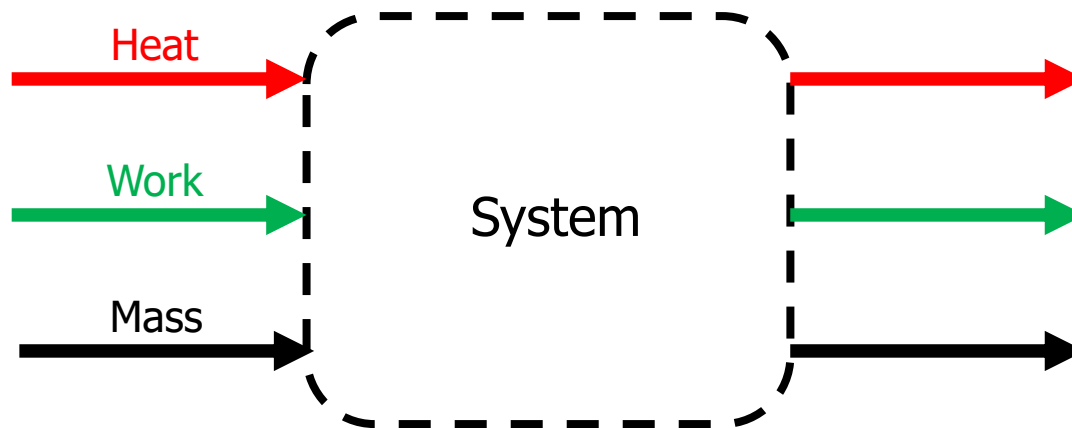
Cryostat Engineering for Helium Superconducting Devices

CERN, 7-9 November 2022



The study of energy and its transformations

- «Macroscopic» thermodynamics allows to say things
 - About materials without knowing their microstructure
 - About machines without knowing the details of their construction
 - About **systems** seen as «black boxes»
- ...just by looking at the flows of **heat**, **work** and mass at their boundary





Thermodynamic systems and equilibrium

- A **system** is what is inside its boundary
- It can exchange heat, work and mass with its environment
 - **Isolated systems** do not exchange heat, work or mass
 - **Closed systems** only exchange heat and work
 - **Open systems** also exchange mass
 - A particular class of open systems are those operating in **steady state**, i.e. without accumulation or depletion of mass inside the system
- A system is in **thermodynamic equilibrium** when no changes occur within it, so that intensive variables (pressure, temperature,...) are homogeneous throughout it



Thermodynamic state and degrees of freedom

- The thermodynamic state of a system at equilibrium can be defined by the values of a limited number of **variables or functions of state**
 - Variables of state: pressure, temperature, chemical potential, magnetization,...
 - Functions of state: energy, enthalpy, entropy,...
- The number of degrees of freedom f of a system at equilibrium is given by **Gibbs' phase rule**

$$f = c + 2 - p$$

- c is the number of chemical components in the system
- p is the number of phases in the system
- Examples
 - Gaseous helium at 1 bar, 290 K: $f = 1 + 2 - 1 = 2$ **bivariant**
 - Liquid helium at saturation: $f = 1 + 2 - 2 = 1$ **monovariant**
 - Liquid air* at saturation: $f = 2 + 2 - 2 = 2$ **bivariant**
 - Any substance at triple point: $f = 1 + 2 - 3 = 0$ **it is a point!**

**Air is supposed to contain only oxygen and nitrogen*



First and Second Principles

In this section, we present the First and Second Principles of thermodynamics and apply them to diverse systems, irrespective of what constitutes these systems.



First Principle: conservation of energy

Closed systems [1/2]

- For a **closed** system

$$dU + dK = dQ + dW$$

- U internal energy, K macroscopic kinetic energy
- Q heat received by system
- W work of external forces on the system, i.e. surface forces (e.g. pressure) and volume forces (e.g. gravity)
- Note 1: this equation defines internal energy (within an additive constant) macroscopically
- Note 2: internal energy can also be defined microscopically

$$U = \sum E_{kin, micro}(T) + \sum E_{pot, micro}$$

- $\sum E_{kin, micro}(T)$ kinetic energy of particles in system
- $\sum E_{pot, micro}$ potential energy of particles in system (interactions between particles)



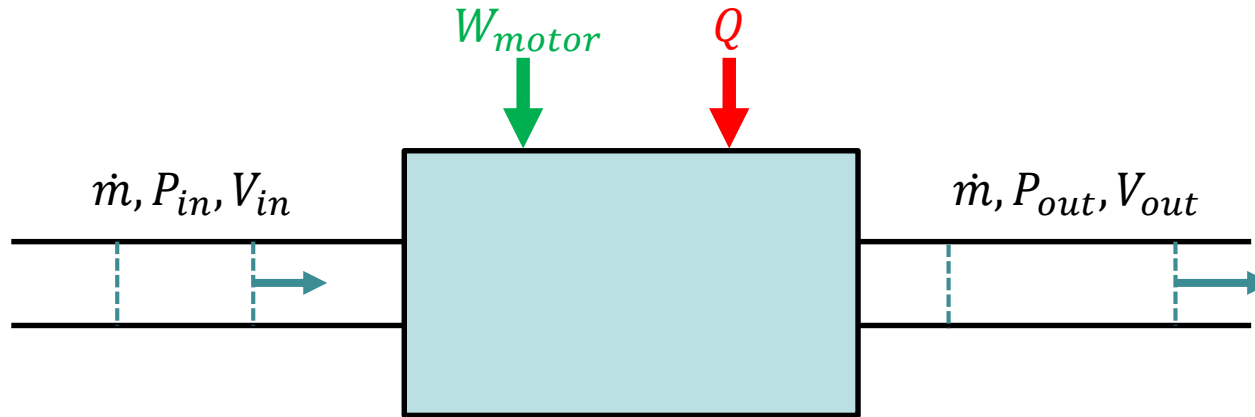
First Principle: conservation of energy Closed systems [2/2]

- For a **closed** system $dU + dK = dQ + dW$
- For a **static fluid** occupying a volume V at pressure P , when the work of gravity can be neglected $dK \equiv 0$
 $dW = -P dV$
 - For an **isochore** (constant volume) process $dQ = dU$
 - *Heat at constant volume equals internal energy rise*
 - *Internal energy is the function of state to be used for isochore processes*
 - For an **isobar** (constant pressure) process $dQ = dU + P dV = dU + d(PV)$
 - Introduce new function of state, **enthalpy** $H \equiv U + PV$
 - Then at constant pressure $dQ = dH$
 - *Heat at constant pressure equals enthalpy rise*
 - *Enthalpy is the function of state to be used for isobar processes (e.g. atmospheric)*
- Introducing **specific heats** $C_V = \left. \frac{dU}{dT} \right|_V$ $C_P = \left. \frac{dH}{dT} \right|_P$
- For a liquid in equilibrium with its vapor, **the latent heat** of vaporization at saturation pressure is $L_v = H_{vap} - H_{liq}$



First Principle: conservation of energy

Open systems in steady-state [1/2]



- Consider an **open system in steady state (i.e. no mass accumulation)**, e.g. the flow of a fluid through a machine (e.g. pump or turbine) operating between inlet pressure P_{in} and outlet pressure P_{out} , receiving or producing «motor» work W_{motor} (respectively counted positively or negatively)
- The first principle applied to a slice of fluid yields

$$\Delta U + \Delta K = Q + P_{in}V_{in} - P_{out}V_{out} + W_{motor}$$

$$\Delta U + \Delta K = Q - \Delta(PV) + W_{motor}$$

$$\Delta H + \Delta K = Q + W_{motor}$$



First Principle: conservation of energy Open systems in steady-state [2/2]

- For an **open system in steady-state**

$$\Delta H + \Delta K = Q + W_{motor}$$

- If there is **no «motor» work** (e.g. flow through a fixed-wall channel)

$$\Delta H + \Delta K = Q$$

- If in addition, the flow is **adiabatic** (e.g. flow through an insulated channel)

$$\Delta H + \Delta K = 0$$

- For small variations in kinetic energy (pipe flow), the process is **isenthalpic**

$$\Delta H = 0$$

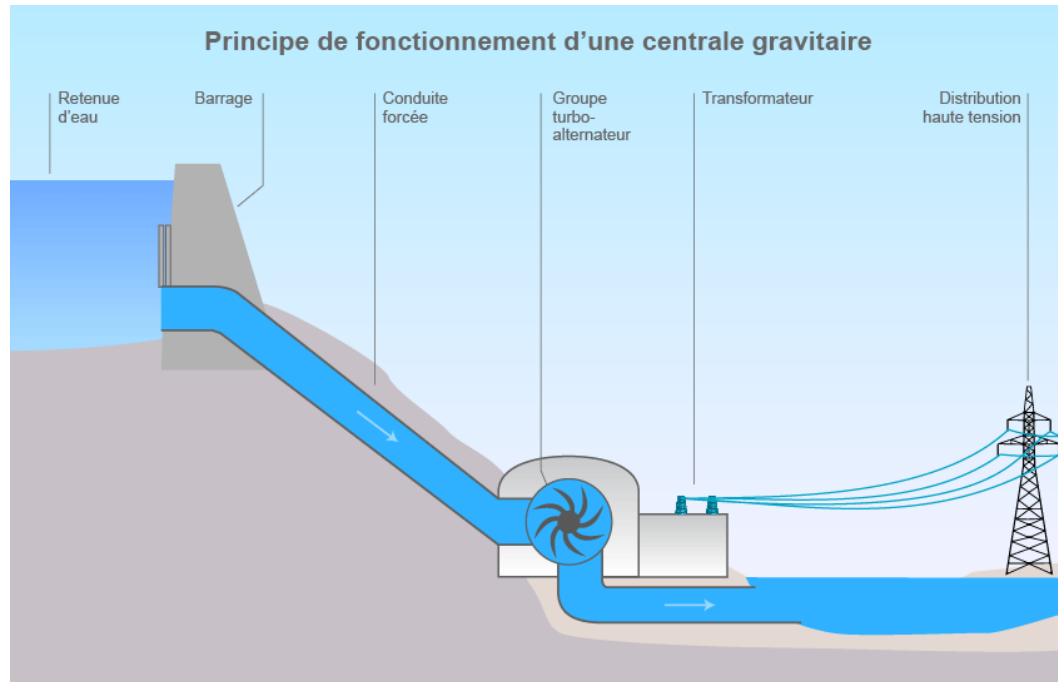
- For adiabatic flow with large change in velocity (e.g. acceleration through a nozzle), the drop in enthalpy is used to accelerate the fluid

$$\Delta H = -\Delta K$$

- *Enthalpy is the function of state to be used for open systems in steady-state*



Thermodynamics tutorial 1: text



- First principle of thermodynamics applied to hydroelectric plant
 1. Define boundary of thermodynamic system (*Hint: make sure you will not have to cope with variations of kinetic energy*)
 2. Write energy conservation of the fluid (water) traversing the system (*Hint: water is assumed non-compressible*)
 3. Doesn't this suggest to introduce a new definition of enthalpy, called I , suited to gravity flow? Rewrite energy conservation using I



Thermodynamics tutorial 2 : text

- Specific heat of solids
 1. Why are C_P and C_V not differentiated for solids?
 2. Estimate numerically their difference for a metal, e.g. aluminium



Thermodynamics tutorial 3 : text

- Helium dewar boiloff and pressurization
 1. Consider a 100-liter He dewar vessel initially filled at 90% with a 1 W heat inleak, vented to atmosphere (1 bar). How long will it take for the liquid level to reach 80%?
 2. At 80% level, the vessel is sealed: what happens? Which function of state is to be used to describe the evolution of the system?
 3. Assuming equilibrium conditions, calculate the evolution of pressure and temperature in the vessel with time



Second Principle

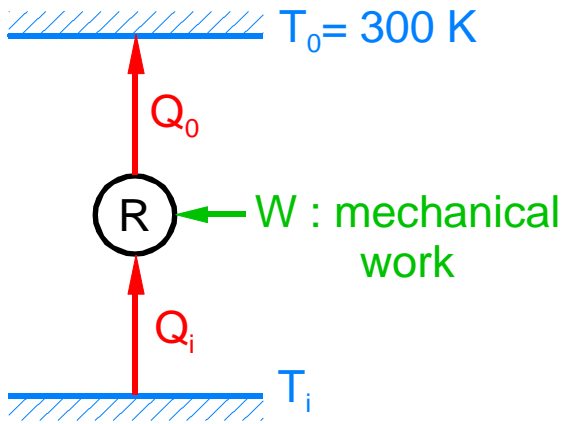
- Consider a closed system exchanging heat quantities ΔQ_i with reservoirs at temperatures T_i
- The Second Principle (Clausius' formulation) states that

$$\sum_i \frac{\Delta Q_i}{T_i} \geq 0$$

- This inequality reduces to equality when the process is **reversible**, i.e. at infinitely small dynamics
- Introduce **entropy** S
$$dS_{rev} = \frac{dQ}{T}$$
- The Second Principle then states that *the entropy of a closed system can only increase*
- Since $dQ = dU + P dV$, and U, P, V, T are functions or variables of state, S_{rev} is also a function of state (defined within an additive constant)
- For real processes
$$\Delta S = \Delta S_{rev} + \Delta S_{irrev} = \frac{\Delta Q}{T} + \Delta S_{irrev}$$
 - Sources of ΔS_{irrev} : heat transfer across finite ΔT , friction, mixing, turbulence,...



Basic thermodynamics of refrigeration



- First principle (Joule) $Q_0 = Q_i + W$

- Second principle (Clausius) $\frac{Q_0}{T_0} \geq \frac{Q_i}{T_i}$

(= for reversible process)

- Hence

$$W \geq T_0 \frac{Q_i}{T_i} - Q_i$$

- This equation can be written in three different ways

$$\left\{ \begin{array}{l} W \geq T_0 \Delta S_i - Q_i \text{ introducing entropy } S \text{ defined by } \Delta S_i = \frac{Q_i}{T_i} \\ W \geq Q_i \left(\frac{T_0}{T_i} - 1 \right) \text{ where } \left(\frac{T_0}{T_i} - 1 \right) \text{ is called the Carnot factor} \\ W \geq \Delta E_i \text{ introducing exergy } E \text{ defined by } \Delta E_i = Q_i \left(\frac{T_0}{T_i} - 1 \right) \end{array} \right.$$



Thermodynamics tutorial 4 : text

- Helium refrigeration and liquefaction work
 1. Calculate the minimum work to produce 1 W isothermal refrigeration at liquid helium temperature (4.2 K), assuming a room temperature of 290 K
 2. The most efficient helium refrigerators have a COP of 220 W/W: what is their efficiency relative to the Carnot cycle?
 3. A liquefier is a non-isothermal refrigerator to which the vaporized helium is returned at room temperature (290 K, 1 bar) instead of cold (4.2 K, 1 bar). Calculate the minimum liquefaction work for 1 g/s liquefaction. How much isothermal refrigeration at 4.2 K can that work produce?

(Hint 1: Latent heat of vaporization of helium at 4.2 K = 20.8 J/g)

(Hint 2: Assume specific heat of helium at 1 bar is constant = 5.2 J/g.K)



From the ideal gas to real fluids

In this section, we characterize the thermodynamic behaviour of substances by their equation of state, starting with the ideal gas and then moving to real fluids. We introduce thermodynamic diagrams as a graphical representation of the equation of state and of the transforms undergone by the fluid.



The ideal gas [1/3]

- Macroscopically, the ideal gas is a substance defined by the equation of state

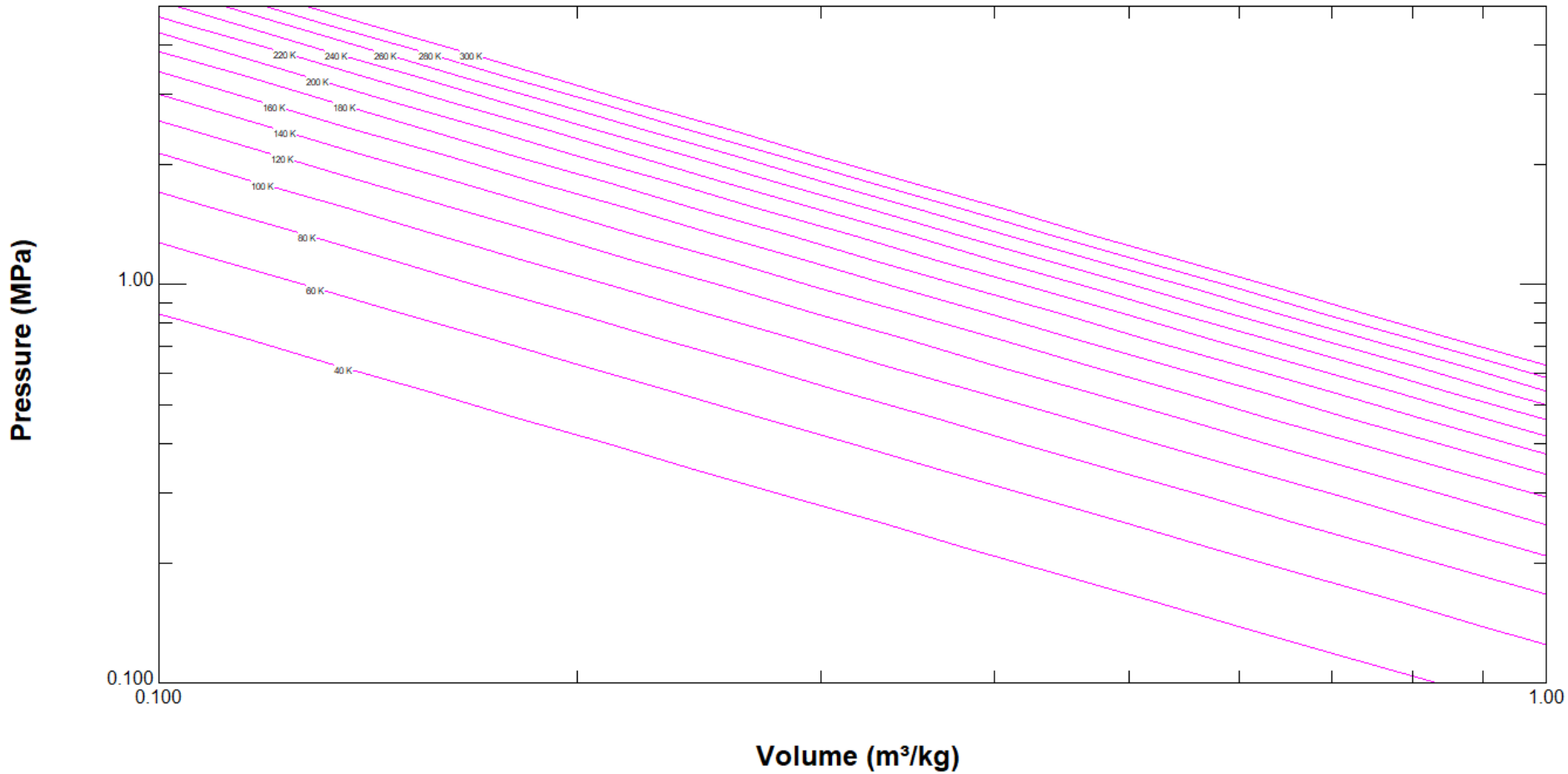
$$P V = n R T$$

- n is the number of moles
 - $R = 8.314 \text{ J}/(\text{K} \cdot \text{mole})$ is the ideal gas constant
- Microscopically, the ideal gas is composed of **point-like** molecules with **no interaction** between them (other than collisions)
- One can show in statistical mechanics that these two definitions are equivalent
- Since $U = \sum E_{kin,micro}(T) + \sum E_{pot,micro}$ the internal energy of the ideal gas reduces to the first term and **depends only on temperature**
- Real gases, composed of molecules with a finite volume and subject to weak attractive interactions (Van der Waals) approach the ideal gas:
 - At low density, when the proper volume of the molecules is negligible as compared to the volume occupied by the gas
 - At high temperature, when the thermal kinetic energy of the molecules is large as compared to the potential energy of their interactions



The Clapeyron P-V diagram of helium

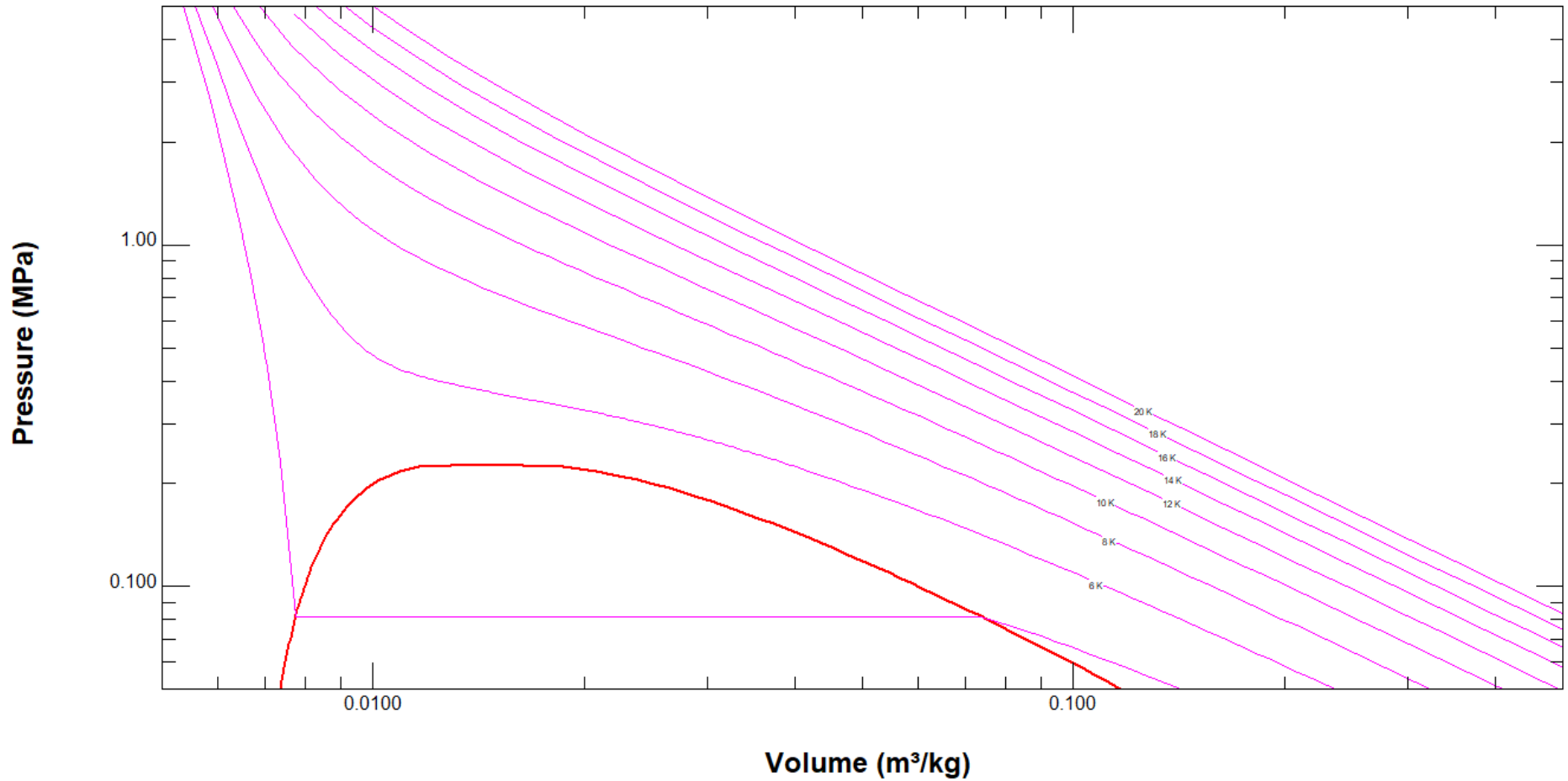
Isotherms 40 – 300 K





The Clapeyron P-V diagram of helium

Isotherms 4 – 20 K





The ideal gas [2/3]

- Internal energy of ideal gas $dU = C_V dT$
 - From statistical mechanics, $C_V = \text{constant}$ does not depend on temperature
 - For a mole of monoatomic ideal gas, $C_V = 3R/2$
 - For a mole of diatomic ideal gas, $C_V = 5R/2$
- Enthalpy of ideal gas $dH = C_p dT$
 $dH = dU + d(PV) = dU + R dT$
 - Enthalpy of the ideal gas **depends only on temperature**
- Mayer's relation $C_p dT = C_V dT + R dT$
 $C_p - C_V = R$
 - $C_p = \text{constant}$ does not depend on temperature
 - For a mole of monoatomic ideal gas, $C_p = 5R/2$
 - For a mole of diatomic ideal gas, $C_p = 7R/2$



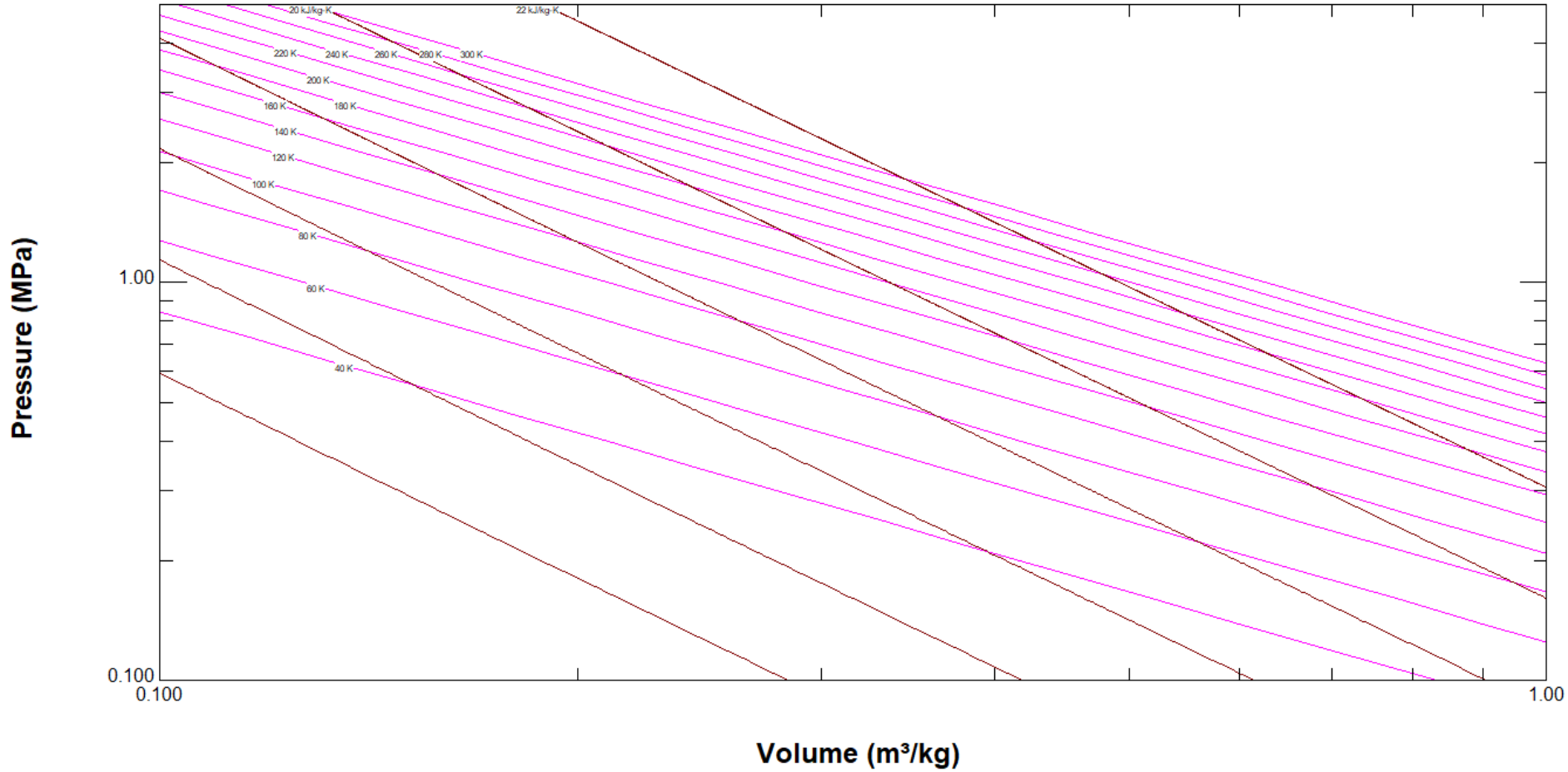
The ideal gas [3/3]

- **Isotherm** transform of an ideal gas $P V = \text{constant}$
 - *The isotherms are hyperbolas on the (P, V) diagram, straight lines on the $\log(P, V)$ diagram*
- **Adiabatic** transform of an ideal gas $dQ \equiv 0$
 - A reversible adiabatic is isentropic $dS \equiv 0$
- Then $dU = C_V dT = dQ - P dV = -P dV$
 $dH = C_P dT = dQ - P dV + d(PV) = dQ + V dP = V dP$
- Introducing $\gamma = C_P/C_V = -V dP/P dV = -d(\text{Ln } P)/d(\text{Ln } V)$
- Integrating $P V^\gamma = \text{constant}$
 - For a monoatomic ideal gas $\gamma = 5/3 \approx 1.67$
 - For a diatomic ideal gas $\gamma = 7/5 \approx 1.4$
 - *The adiabats (isentrops) cross the isotherms with a higher slope, the ratio of the slopes is γ*
- Adiabatic transforms of real gases are approximated with the **polytropic** law
 $P V^n = \text{constant}$ with n polytropic index



The Clapeyron P-V diagram of helium

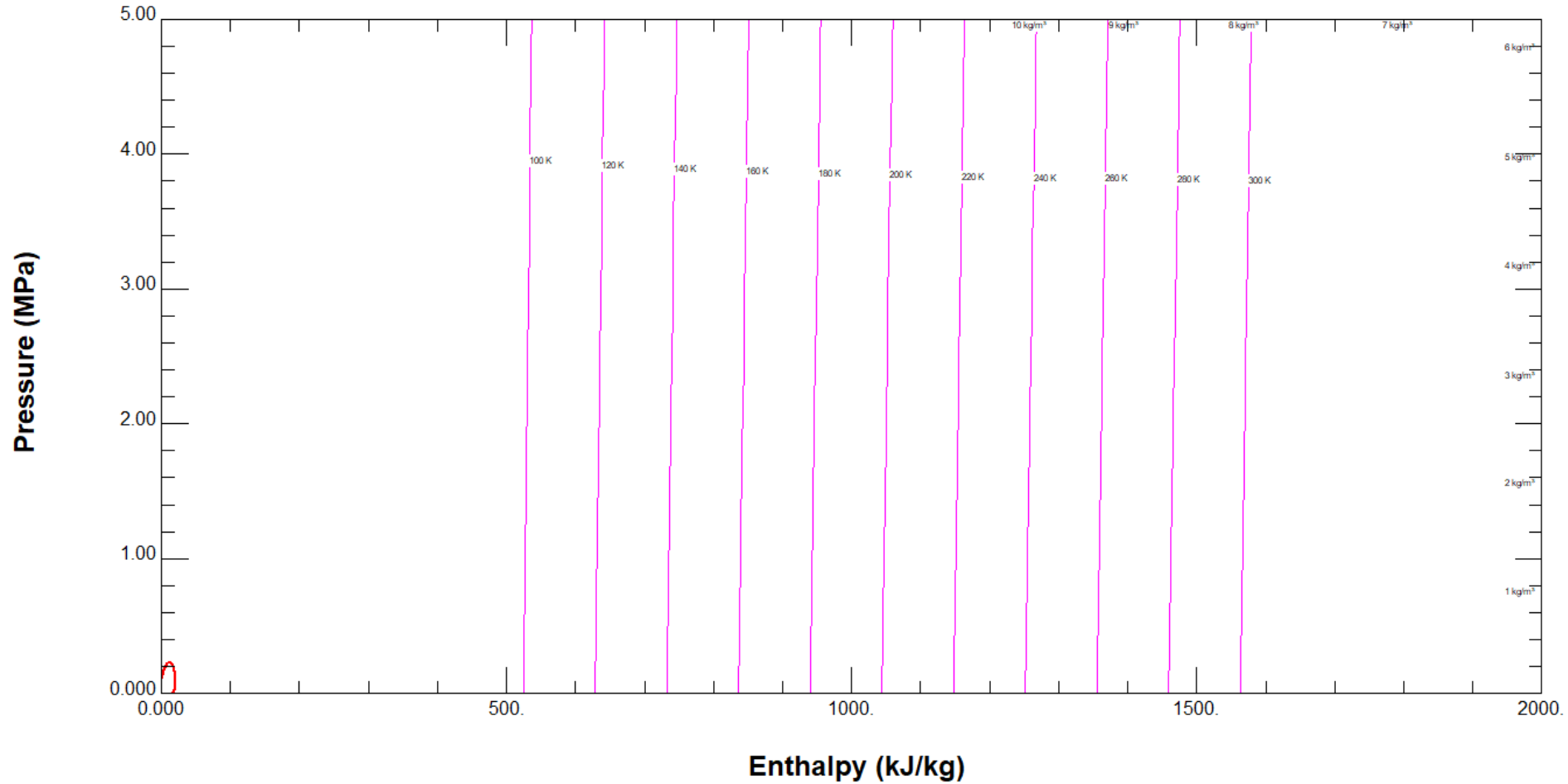
Isotherms 40 – 300 K, isentrops 12 – 22 J/kg.K





The P-H diagram of helium

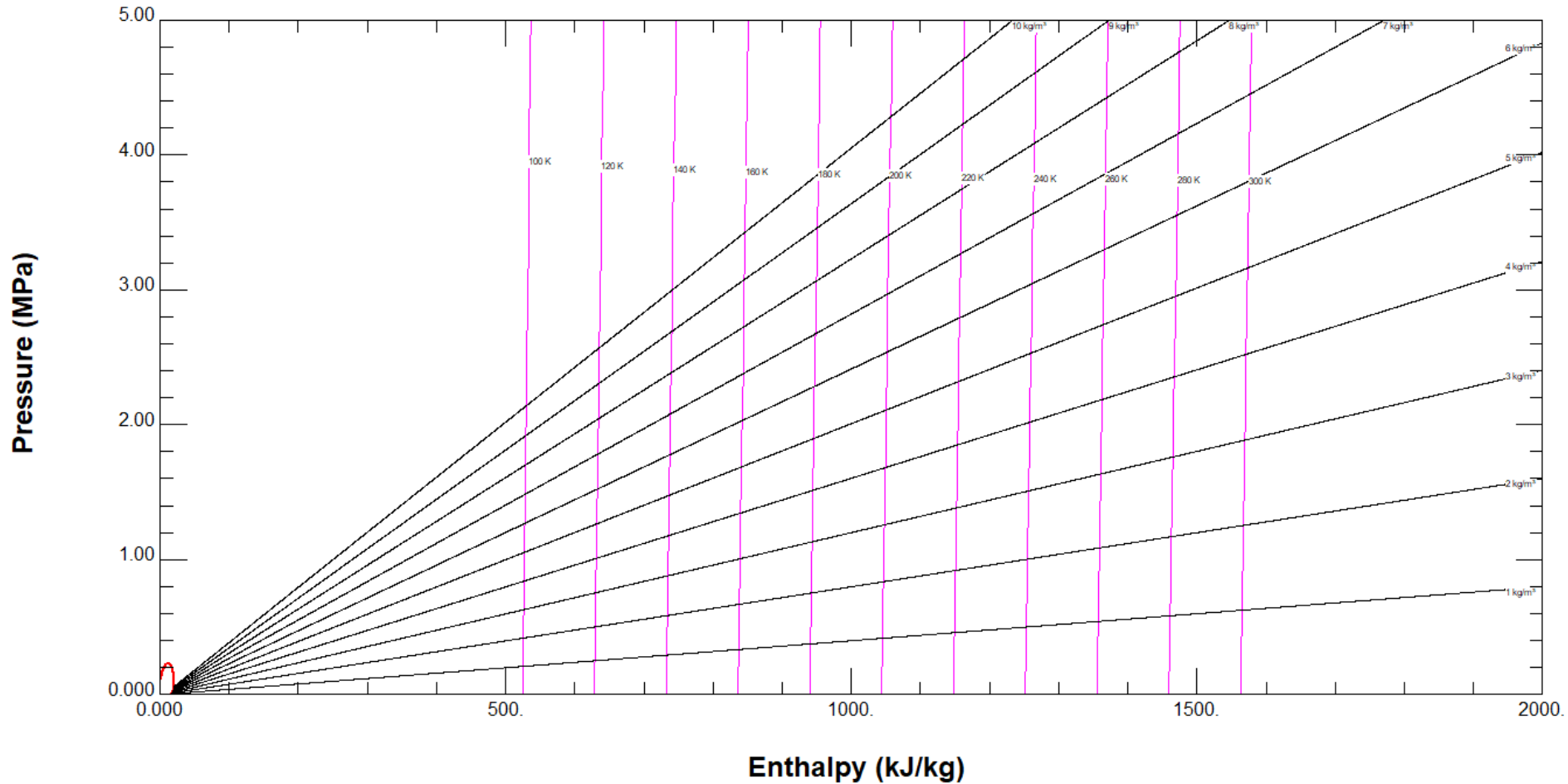
Isotherms 100 – 300 K





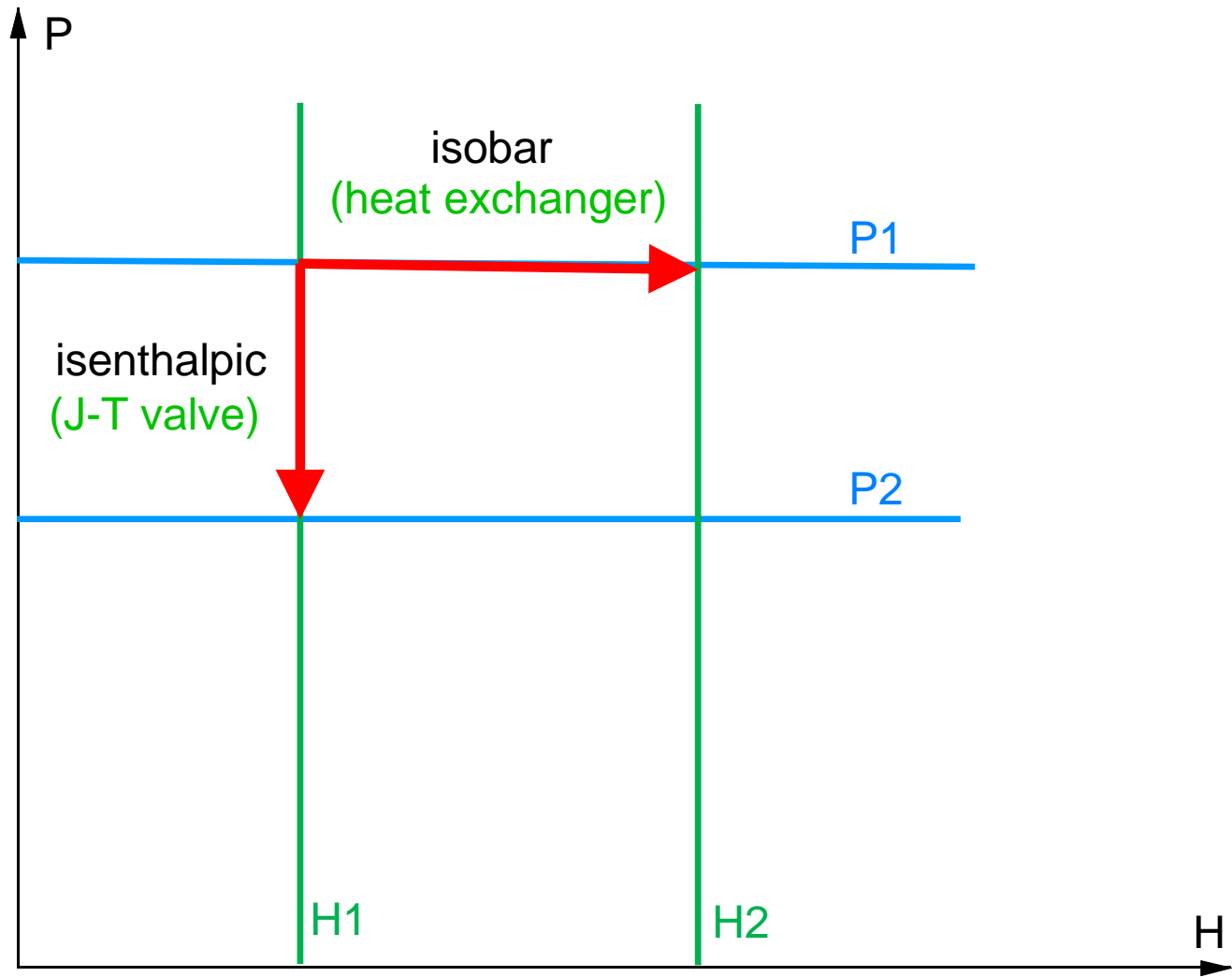
The P-H diagram of helium

Isotherms 100 – 300 K, isochores 1-10 kg/m³





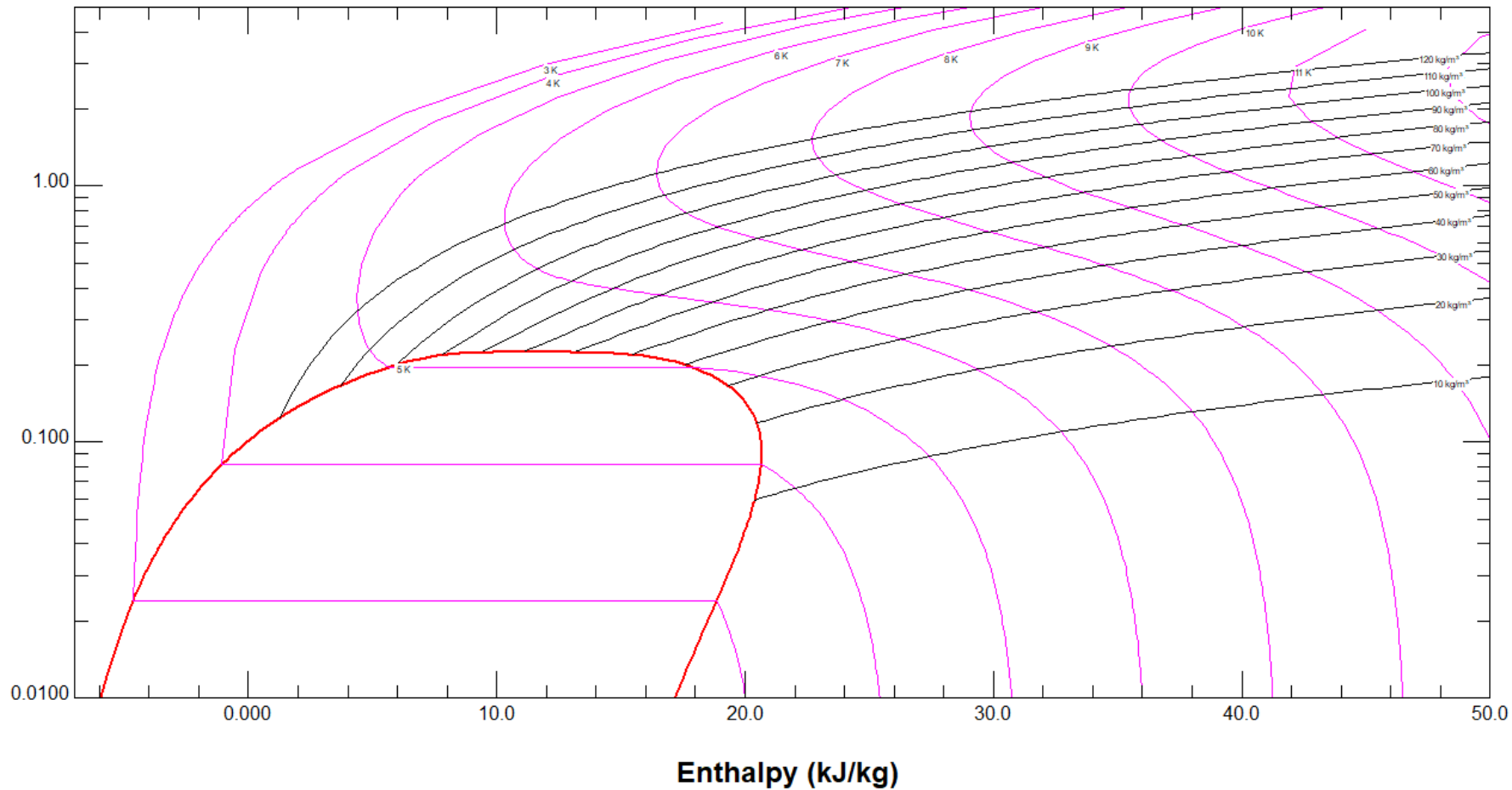
When to use the P-H diagram





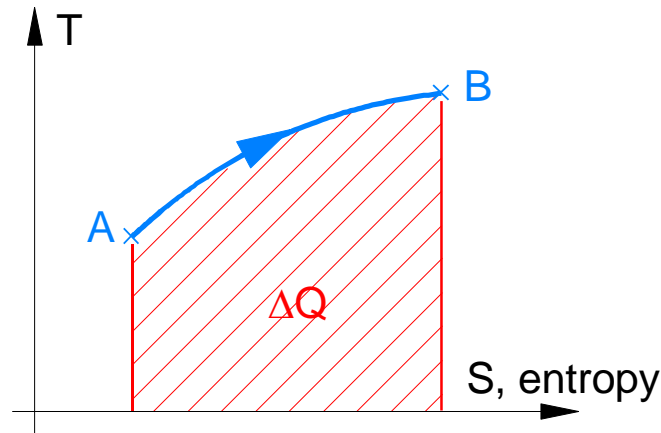
The P-H diagram of helium

Isotherms 3 – 12 K, isochores 10 – 120 kg/m³





The T-S diagram

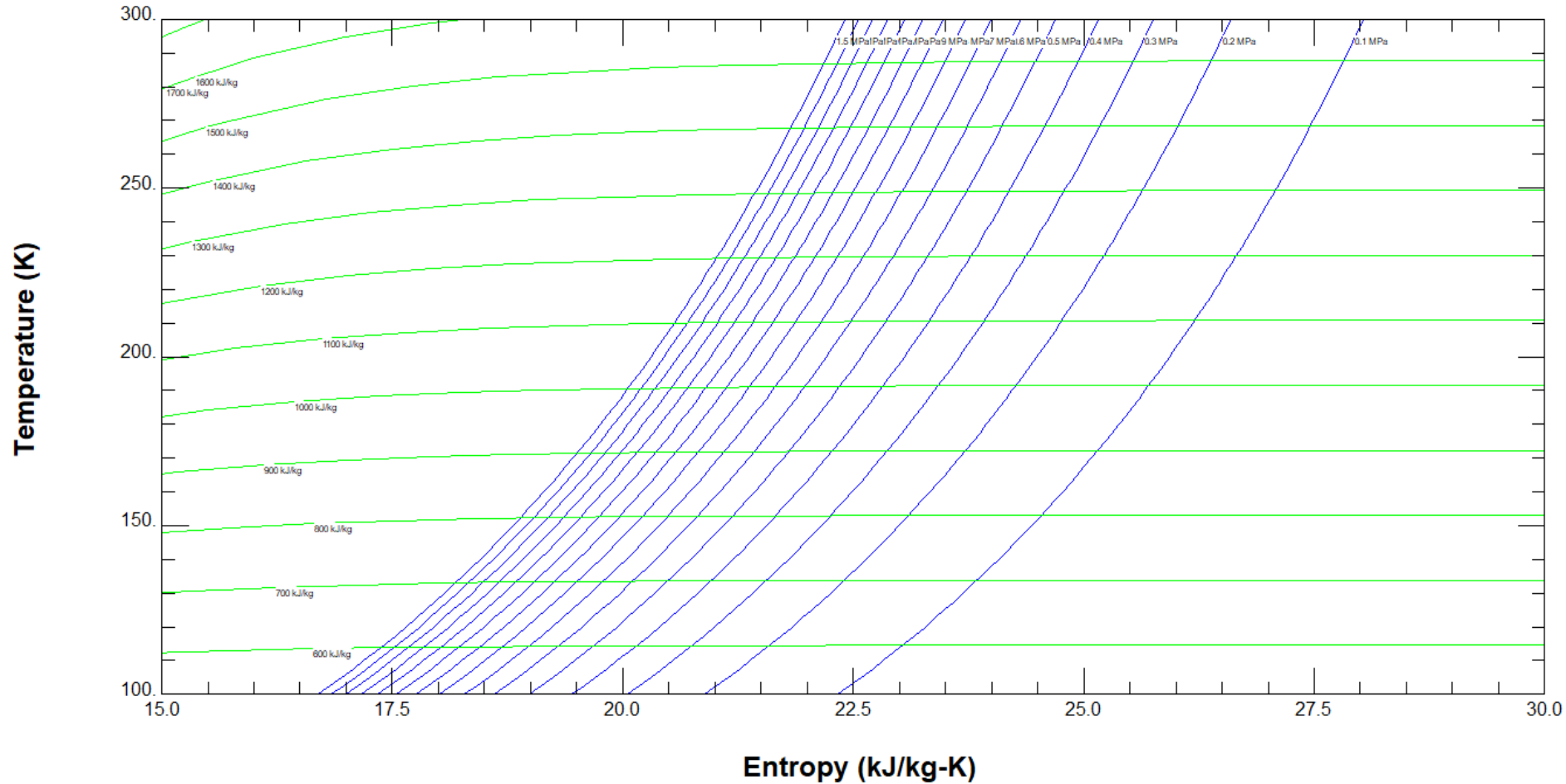


- Characteristic of the temperature-entropy diagram
 - Consider the thermodynamic transform from A to B, involving heat transfer ΔQ
 - If it is reversible $\Delta Q = \int_A^B T dS$
 - ΔQ is proportional to the area under the curve in the temperature-entropy diagram
- For the ideal gas
 - Isenthalps \equiv isotherms are horizontal lines
 - Isochores $dU = C_V dT = dQ$ hence $dS = dQ/T = C_V dT/T$ and $T = T_0 \exp(S/C_V)$
 - Isobars $dH = C_P dT = dQ$ hence $dS = dQ/T = C_P dT/T$ and $T = T_0 \exp(S/C_P)$
 - Isochores and isobars are exponentials, isochores steeper than isobars



The (T, S) diagram of helium

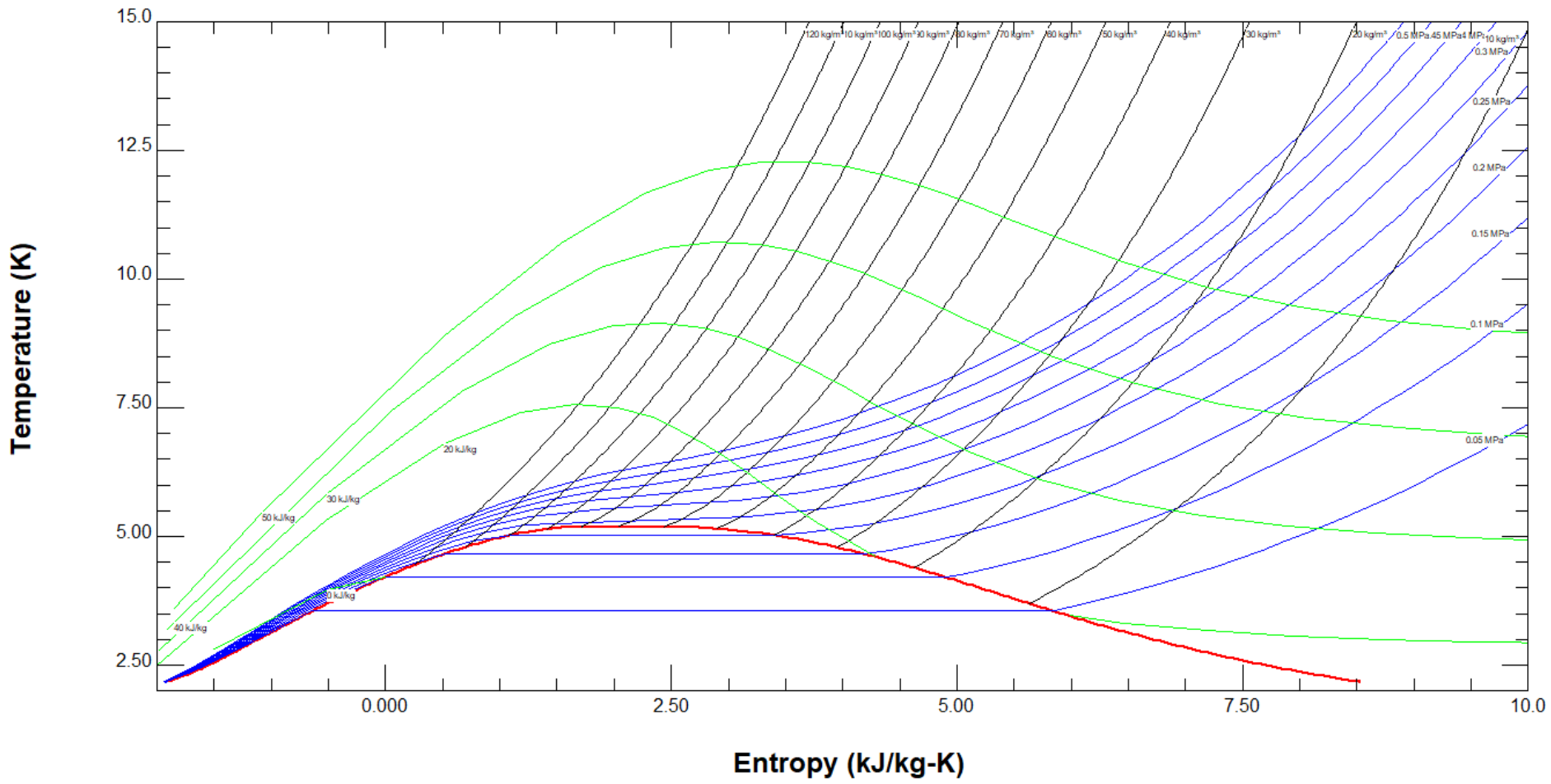
Isobars 0.1-1.5 MPa, isenthalps 500-2000 kJ/kg





The (T, S) diagram of helium

Isobars 0.05 - 0.5 MPa, isochores 10 - 120 kg/m³, isenthalps 0 - 50 kJ/kg





When to use the T-S diagram

