Thermodynamica 1

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college 5 – boek hoofdstuk 3

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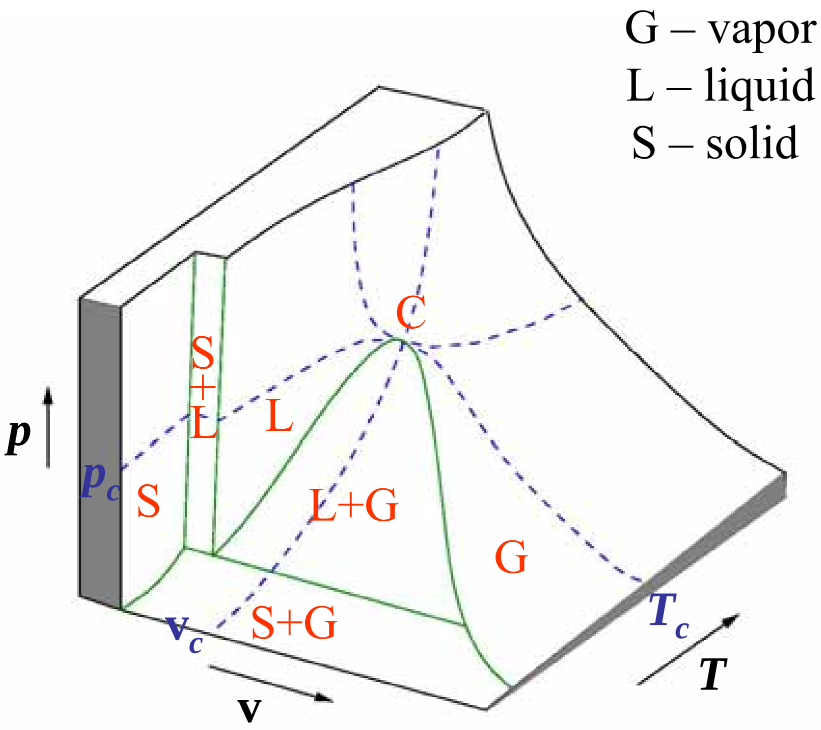
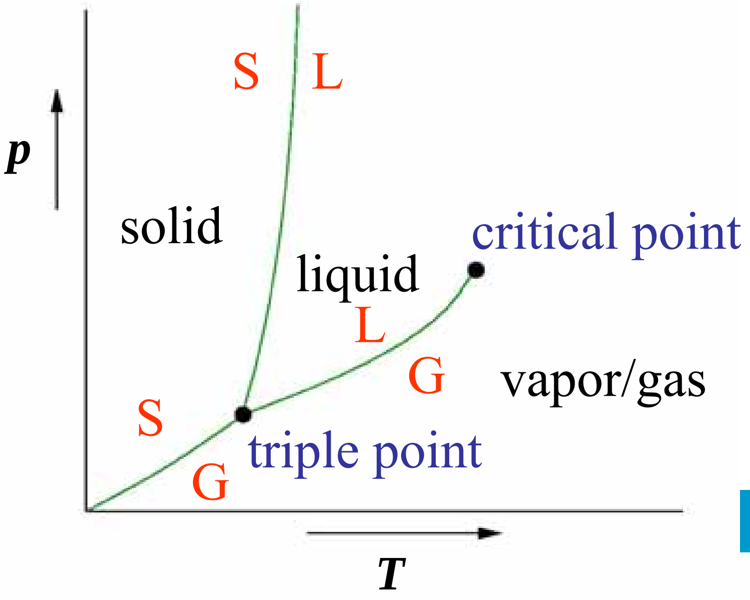
summary lecture 4

- properties of matter
- p-V-T surface
- isobar, isotherm, isochor
- phase transition
- coexisting phases
- working with tables, interpolation





equation of state of **Ideal Gases**

The intensive properties $\{p, v, T\}$ of matter (gas, liquid, solid) are **not** independent of one another. The relation between them is called **equation of state**

The simplest equation of state is the **ideal gas equation of state**

It was found in stages, by realizing that $pV = C(n, T)$

if the Kelvin-temp. scale is used, it was seen that $pV = C(n)T$

the final equation of state is

$$pV = n\bar{R}T$$

universal gas constant

$$\bar{R} = 8.314471 \frac{J}{mol\,K}$$

p	pressure $[Pa]$
V	volume $[m^3]$
T	temperature $[K]$
n	amount of substance $[mol]$

1 mol contains $N_A = 6.0221367 \times 10^{23}$ molecules

equation of state of **Ideal Gases**

$$pV = n\bar{R}T \qquad p\bar{v} = \bar{R}T \qquad \bar{v} = \frac{V}{n}$$

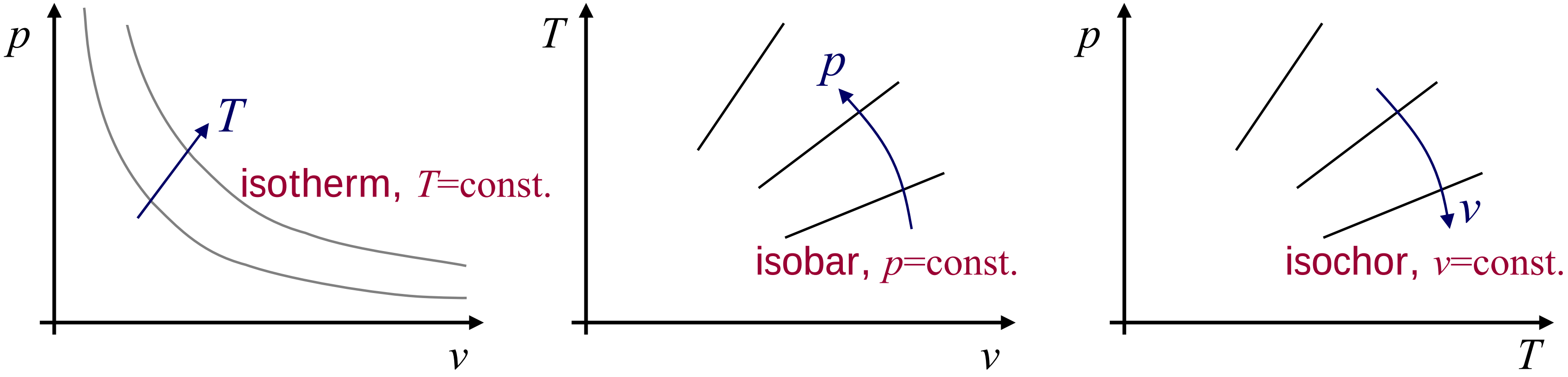
$$\bar{R} = 8.314471 \frac{J}{mol\,K}$$

p	pressure $[Pa]$
V	volume $[m^3]$
T	temperature $[K]$
n	amount of substance $[mol]$

1 mol contains $N_A = 6.0221367 \times 10^{23}$ molecules

the “iso”-diagrams for ideal gases

The relation between 2 of the 3 properties $\{p,v,T\}$ can be visualized in state diagrams



relevance of the ideal gas model

- The ideal gas state is a limit for gases of low density
- Every real component approaches ideal gas behavior for pressures $p \rightarrow 0\ bar$ and $\rho \rightarrow 0\ kg/m^3$
- Molecular interpretation: a gas shows ideal gas behavior, when the molecular interactions do not play a role ($\Rightarrow$ for low densities and/or high temperature)

dealing with “real” gases

compressibility factor: $Z = \dfrac{p\overline{\mathrm{v}}}{\overline{R}T}$

ideal gas limit: $\lim\limits_{p\to 0} Z = 1$

reduced pressure and
reduced temperature: $p_{\mathrm{R}} = \dfrac{p}{p_c}, \quad T_{\mathrm{R}} = \dfrac{T}{T_c}$

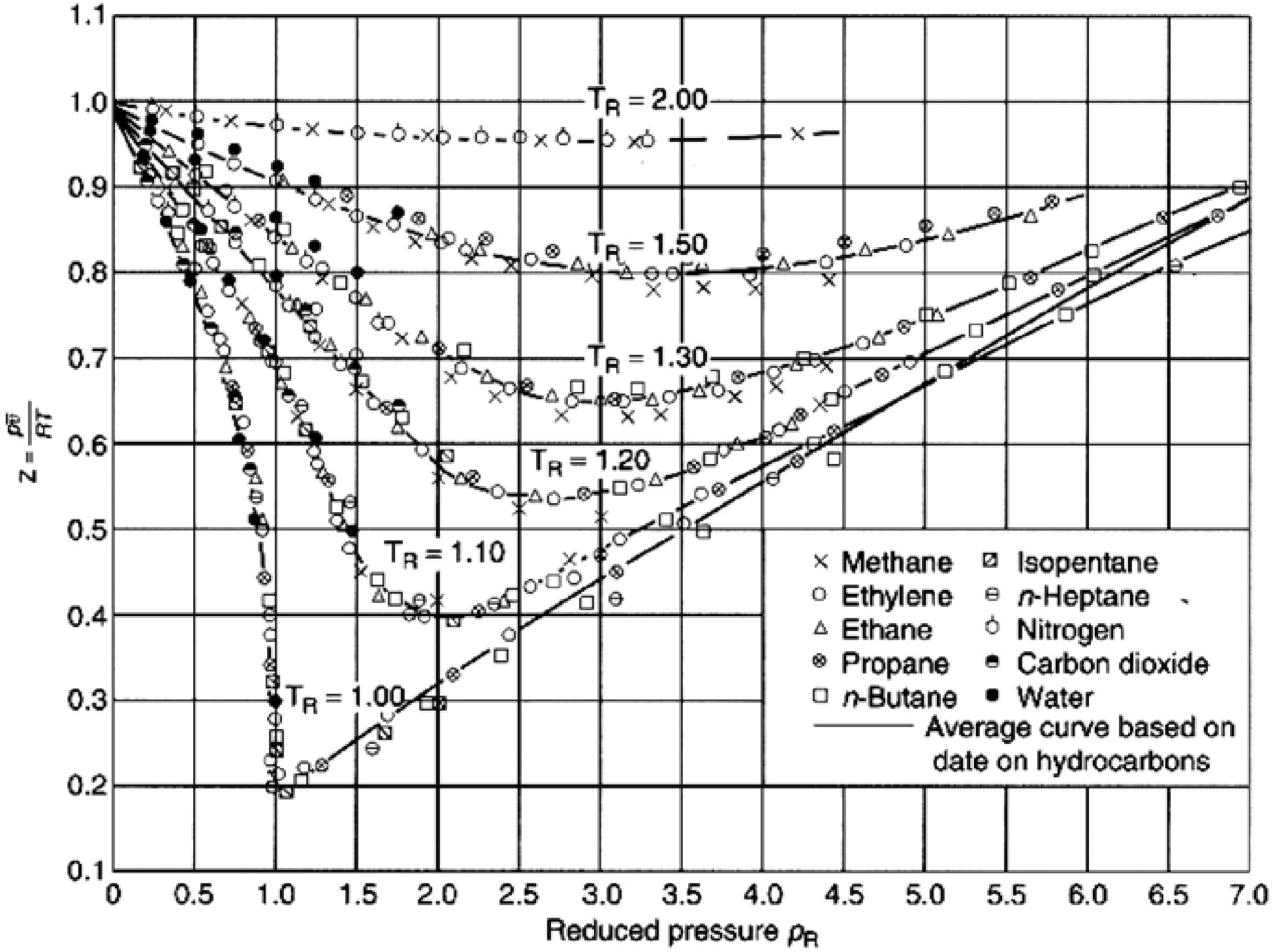


Figure 3.11 Generalized compressibility chart for various gases

examples of equations of state

- Ideal gas equation of state

$$Z = \frac{p\overline{\mathrm{v}}}{\overline{R}T} = 1$$

- Virial equation of state (for non-ideal gasses)

$$Z = \frac{p\overline{\mathrm{v}}}{\overline{R}T} = 1 + B(T)p + C(T)p^2 + D(T)p^3 + \ldots\ldots..$$

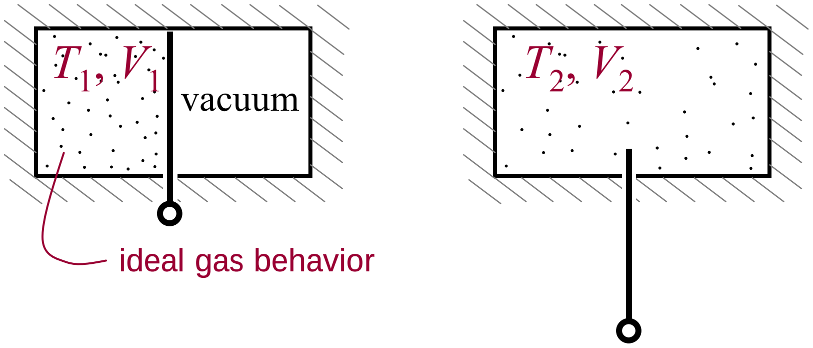
- Van der Waals equation of state (for non-ideal gasses)

$$\left(p + \frac{n^2 a}{V^2}\right)\left(V - nb\right) = n\overline{R}T$$

the **internal energy** of an ideal gas

experiment of Joule and Thomson

measurement: $T_1=T_2=T$!



first law: $$dU = \delta Q - \delta W$$

$$\Delta_{12}U = \underbrace{\cancel{\Delta_{12}Q}}_{=0} - \underbrace{\cancel{\Delta_{12}W}}_{=0}$$

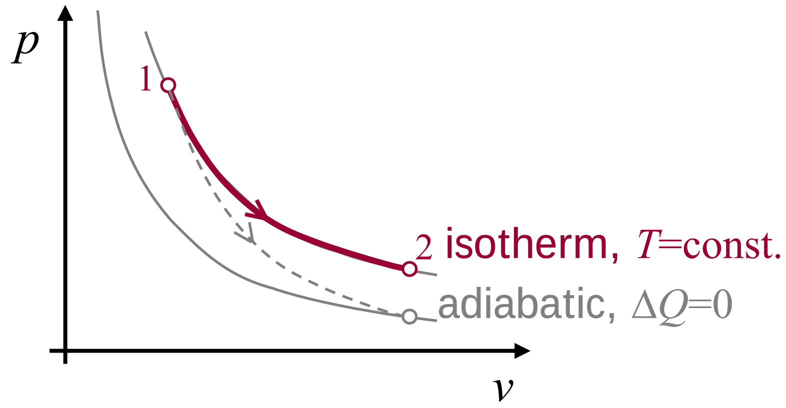
$$\Rightarrow \quad \Delta_{12}U = 0$$

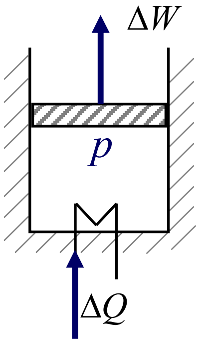
$$\Rightarrow \quad U_2 - U_1 = U(T,V_2) - U(T,V_1) = 0$$

$$\Rightarrow \quad u(T,v_2) - u(T,v_1) = 0 \qquad \text{with} \qquad v_2 \neq v_1$$

$\Rightarrow$ we conclude that u is only a function of temperature $u(T)$ **for an ideal gas**

isothermal expansion of an ideal gas





note: an isothermal process requires providing energy in form of heat during expansion, otherwise the temperature would decrease

first law

$$\underbrace{\cancel{dU}}_{=0} = \delta Q - \underbrace{\cancel{\delta W}}_{= pdV}$$

because $u(T)$
and T=const.

$$p = \frac{n\bar{R}T}{V}$$ ideal gas law

$$\Rightarrow \Delta_{12}Q = \Delta_{12}W = \int_{V_1}^{V_2} pdV = n\bar{R}T \int_{V_1}^{V_2} \frac{1}{V} dV = n\bar{R}T \ln \frac{V_2}{V_1}$$

polytropic expansion

$$pV^n = \text{constant (with n} \neq 1)$$

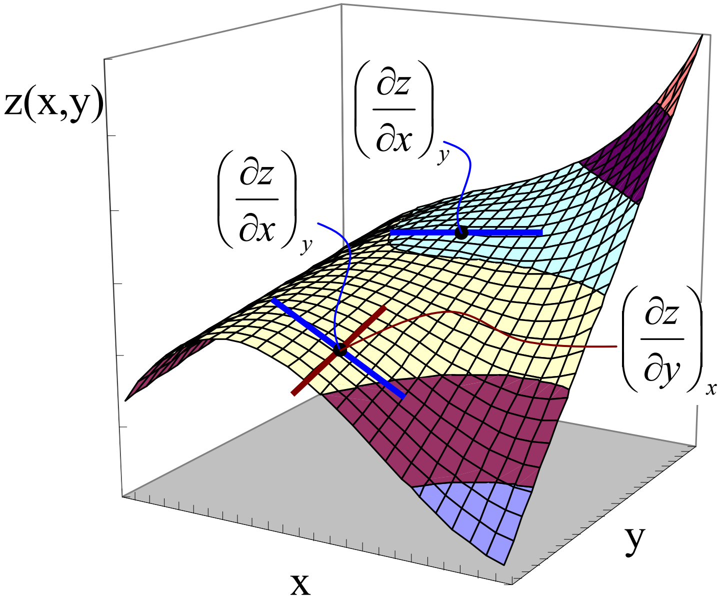
$$\Delta_{12}W = \int_{V_1}^{V_2} p\,dV = \frac{p_2V_2 - p_1V_1}{1-n}$$

Math: Differential relations of multivariable functions

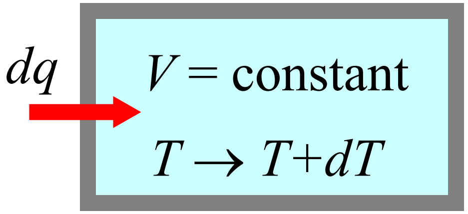
- consider a differentiable function $z(x,y)$
- Think of z as the height coordinate in the Swiss Alps, and x and y are the northerly direction and the westerly direction, respectively
- The total differential is

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

- $(\partial z/\partial x)_y$ is the slope with which the height changes with a change dx in x-direction. Subscript y is for: "in direction of constant y"
- Note, that $(\partial z/\partial x)_y$ is a function of y, as seen in the illustration



Specific heat at constant volume



- For an ideal gas: $u(T,v) = u(T)$

- How does $u(T)$ change with T ?

- Recall the first law: $du = \delta q - \delta w = \delta q - pdv$

- At constant volume: $du = \delta q$

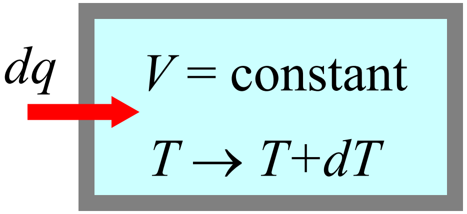
- Definition of heat capacity at constant volume (here: in units of [$J\,mol^{-1}\,K^{-1}$])

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v$$

- c_v : the amount of heat that needs to be added to increase the temperature of 1 mol material by 1 Kelvin, while keeping the **volume** constant. Definition is valid also for non-ideal gasses.

Specific heat at constant volume

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v$$



- For an ideal gas,

$$c_v = c_v(T)$$

- Usually:

$$c_V = a + bT + cT^2 + \ldots\ldots$$

- Energy change at constant volume upon heating:

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} \left(\frac{\partial u}{\partial T}\right)_v dT = \int_{T_1}^{T_2} c_v dT$$

Energy change upon heating at constant V

$$\text{suppose: } c_V = a + bT$$

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} \left(\frac{\partial u}{\partial T} \right)_v dT = \int_{T_1}^{T_2} c_v dT = \int_{T_1}^{T_2} (a + bT) dT =$$

$$\left[aT + \frac{1}{2} bT^2 \right]_{T_1}^{T_2} = a(T_2 - T_1) + \frac{b}{2}\left(T_2{}^2 - T_1{}^2\right)$$

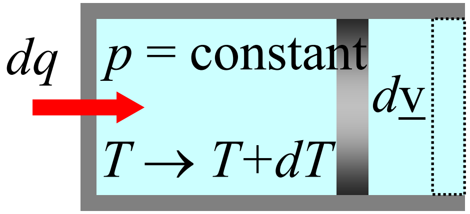
The Enthalpy

$$H \equiv U + pV$$

$$h \equiv u + pv$$

$$dh = du + d\left(pv\right) = du + pdv + vdp$$

adding heat while keeping the pressure constant



- Recall the first law: $du = \delta q - \delta w = \delta q - pdv$

- Enthalpy: $H \equiv U + pV$ $\qquad h \equiv u + pv$

- First law in terms of enthalpy:

$$dh = \delta q + vdp$$

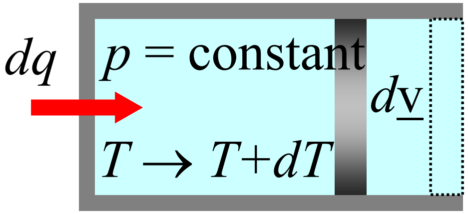
- Adding heat at constant pressure $dh = \delta q$

- Definition of heat capacity at constant pressure: (here: in units of [$J\ mol^{-1}\ K^{-1}$])

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_p$$

specific heat at constant pressure

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_p$$



- For an ideal gas,

$$c_p = c_p(T)$$

- Usually:

$$c_p = a + bT + cT^2 + \ldots\ldots$$

- Enthalpy change at constant pressure upon heating:

$$\Delta h = h_2 - h_1 = \int_{T_1}^{T_2} \left(\frac{\partial h}{\partial T}\right)_p dT = \int_{T_1}^{T_2} c_p dT$$

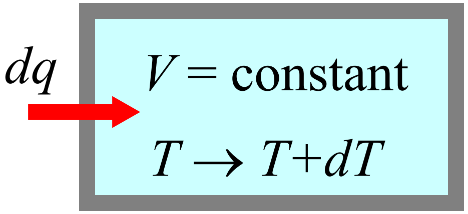
heating at constant volume or pressure

- At constant **volume**: $du = \delta q$

- Definition of heat capacity at constant **volume** (here: in units of [$J\,mol^{-1}\,K^{-1}$])

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v$$

- c_v : the amount of heat that needs to be added to increase the temperature of 1 mol material by 1 Kelvin, while keeping the **volume** constant

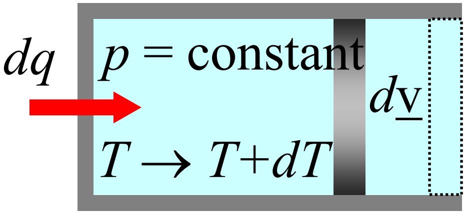


- At constant **pressure**: $dh = \delta q$

- Definition of heat capacity at constant **pressure** (here: in units of [$J\,mol^{-1}\,K^{-1}$])

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_p$$

- c_p : the amount of heat that needs to be added to increase the temperature of 1 mol material by 1 Kelvin, while keeping the **pressure** constant



Instructions

- Chapters 1,2,3 have been treated
- we discussed and illustrated the ideal gas law – read thoroughly in book !!!
- memorize the definition of enthalpy
- memorize the first law of closed systems in terms of the enthalpy
- understand that $u(T)$ and that $h(T)$ for ideal gas
- understand the heat capacity c_v and c_p what does it tell you?
- make exercises concerning ideal gasses and non-ideal gasses; (compressibility factor Z, use ±5% deviation as a good approximation to the ideal gas model).

relation between c_p and c_v for an ideal gas

$$h = u + pv = u + \overline{R}T$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\partial\left(u + \overline{R}T\right)}{\partial T}\right)_P = c_v + \overline{R}$$

adiabatic expansion of an ideal gas (c_v = constant)

$$du = \delta q - pdv = -pdv$$

$$c_v dT = -\frac{\overline{R}Tdv}{v}$$

$$c_v \frac{dT}{T} = -\overline{R}\frac{dv}{v}$$

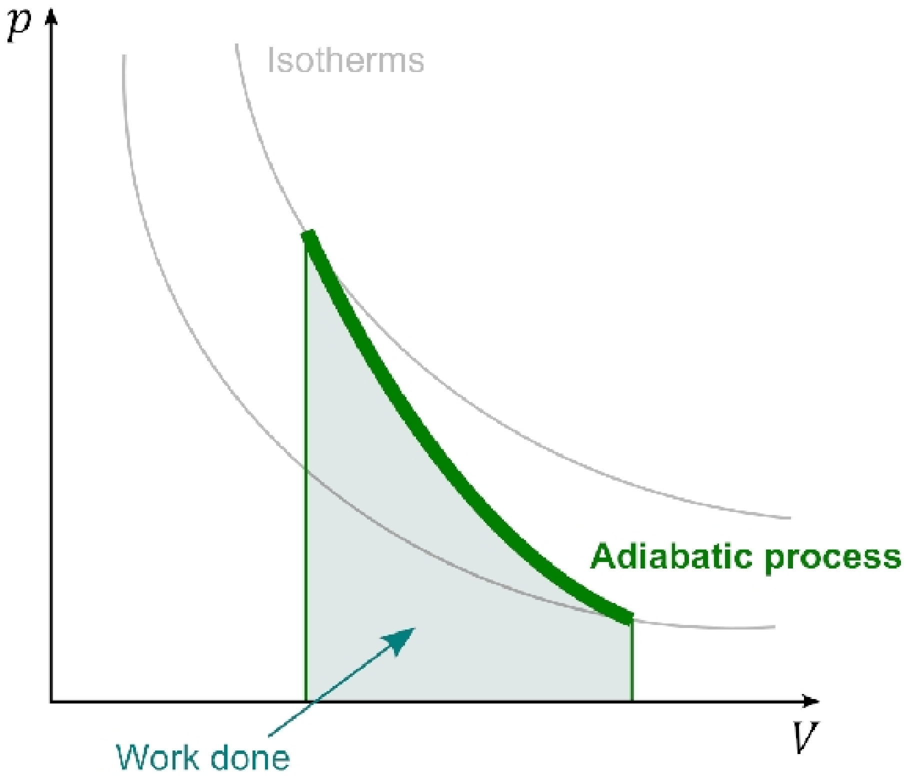
$$c_v \int_{T_1}^{T_2} \frac{dT}{T} = -\overline{R}\int_{v_1}^{v_2} \frac{dv}{v}$$

$$c_v \ln\frac{T_2}{T_1} = -\overline{R}\ln\frac{v_2}{v_1}$$

after some math...

$$pv^{\kappa} = \text{constant (with } \kappa = \frac{c_p}{c_v}\text{)}$$

Adiabatic Expansion



$$pv^{\kappa} = \text{constant} \qquad \kappa = \frac{c_p}{c_v}$$

Clement & Desormes' Experiment (1)

Op druk gebrachte fles is toestand 1; na isochore expansie is toestand 2. Na de adiabatisch veronderstelde snelle expansie juist voor het sluiten van de kraan is de druk p_0 (omgevingsdruk)

$$p_1 = p_0 + \rho g h_1 \quad (1) \Leftrightarrow p_0 = p_1 - \rho g h_1 \quad (1a)$$

$$p_2 = p_0 + \rho g h_2 \quad (2) \Rightarrow p_2 = (p_1 \overset{1a}{-} \rho g h_1) + \rho g h_2 = p_1 - (h_1 - h_2)\rho g \quad (2a)$$

Na op druk brengen van de fles volgt adiabatische expansie:

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \qquad (3)$$

Gas na op druk brengen en na de isochore expansie bereikt uiteindelijk dezelfde T ⇒

$$p_1 V_1 = p_2 V_2 \qquad (4) \qquad \Leftrightarrow \qquad \left(\frac{V_1}{V_2}\right)^{\gamma} = \left(\frac{p_2}{p_1}\right)^{\gamma} \qquad (5)$$

Met (3) en $V_2 = V_0$ volgt dan:

$$\left(\frac{V_1}{V_2}\right)^{\gamma} = \left(\frac{p_0}{p_1}\right) \qquad (6)$$

Clement & Desormes' Experiment (2)

Uit (5) en (6) volgt: $\left(\frac{p_2}{p_1}\right)^{\gamma}=\left(\frac{p_0}{p_1}\right)$ (7) $\Leftrightarrow$ $\gamma=\frac{\ln\left(\frac{p_0}{p_1}\right)}{\ln\left(\frac{p_2}{p_1}\right)}$ (7a)

Verdere vereenvoudiging mogelijk als p niet teveel van p_0 afwijkt.

(7) en (1a) $\Rightarrow$ $\left(\frac{\left(p_1\text{-}\left(h_1\text{-}h_2\right)\rho g\right)}{p_1}\right)^{\gamma}=\left(\frac{p_1-\rho g h_1}{p_1}\right)$ (8)

$$\left(1-\frac{\left(h_1\text{-}h_2\right)\rho g}{p_1}\right)^{\gamma}=1-\left(\frac{\rho g h_1}{p_1}\right) \qquad (9)$$

Als $(h_1\text{-}h_2)\rho g/p_1$ <<1 dan mag (9), aangezien geldt voor een functie $(1+x)^{\alpha}\approx 1+\alpha x$ met x<<1 (volgt uit f(x) = f(0+x) $\approx$ f(0)+x f'(0)), benaderd worden met

$$1-\gamma\frac{\left(h_1\text{-}h_2\right)\rho g}{p_1}=1-\left(\frac{\rho g h_1}{p_1}\right) \quad\Leftrightarrow\quad \gamma=\left(\frac{h_1}{h_1-h_2}\right) \qquad (10)$$