Thermodynamica 1

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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

G – vapor
L – liquid
S – solid

$p$ $T$

$v$

$T_c$ $p_c$

$S+G$ $S+L$

$S$ $L$ $G$ $S+G$ $S+L$

$C$ $L+G$

$p$ $T$

solid liquid vapor/gas
critical point triple point
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**

\[
pV = C(n,T) \quad pV = C(n)T
\]

It was found in stages, by realizing that if the Kelvin-temp. scale is used, it was seen that

the final **equation of state** is

\[
pV = n\bar{R}T
\]

universal gas constant

\[
\bar{R} = 8.314471 \frac{J}{mol \text{ } K}
\]

\begin{align*}
p & \quad \text{pressure [Pa]} \\
v & \quad \text{volume [m}^3\text{]} \\
T & \quad \text{temperature [K]} \\
n & \quad \text{amount of substance [mol]}
\end{align*}

1 mol contains \( N_A = 6.0221367 \times 10^{23} \) molecules
equation of state of Ideal Gases

\[ pV = n\bar{R}T \quad p\bar{v} = \bar{R}T \quad \bar{v} = \frac{V}{n} \]

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

- \( p \) 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 $p \to 0 \text{ bar}$ and $\rho \to 0 \text{ kg/m}^3$
- 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: \[ Z = \frac{p \bar{V}}{RT} \]

ideal gas limit: \[ \lim_{p \to 0} Z = 1 \]

reduced pressure and reduced temperature: \[ p_R = \frac{p}{p_c}, \quad T_R = \frac{T}{T_c} \]
Figure 3.11  Generalized compressibility chart for various gases
examples of equations of state

• Ideal gas equation of state

\[ Z = \frac{p\bar{V}}{RT} = 1 \]

• Virial equation of state (for non-ideal gases)

\[ Z = \frac{p\bar{V}}{RT} = 1 + B(T)p + C(T)p^2 + D(T)p^3 + \ldots \]

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

\[ \left( p + \frac{n^2a}{V^2} \right)(V - nb) = n\bar{RT} \]
the internal energy of an ideal gas

experiment of Joule and Thomson

measurement: \( T_1 = T_2 = T \)

first law: \( dU = \delta Q - \delta W \)

\[
\Delta_{12} U = \Delta_{12} Q - \Delta_{12} W \\
\begin{cases} 
\Delta_{12} Q = 0 \\
\Delta_{12} W = 0 
\end{cases}
\]

\( \Rightarrow \quad \Delta_{12} U = 0 \)

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

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

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

first law

\[ dU = \delta Q - \delta W = 0 \]

because \( u(T) \) and \( T = \text{const.} \)

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

note: an isothermal process requires providing energy in form of heat during expansion, otherwise the temperature would decrease
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 \( \text{[}J\text{mol}^{-1}\text{K}^{-1}\text{]} \))

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

• \( c_v \): 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 gases.
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:

\[ c_V = a + bT + cT^2 + \ldots \]

• 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

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

\[ H \equiv U + pV \]

\[ h \equiv u + pv \]

\[ dh = du + d(pv) = du + pdv + vdp \]
adding heat while keeping the pressure constant

• Recall the first law: \[ du = \delta q - \delta w = \delta q - pdv \]

• Enthalpy: \[ H \equiv U + pV \quad h \equiv u + pv \]

• 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:

\[ c_p = a + bT + cT^2 + \ldots \]

- 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 \([J \text{ mol}^{-1} \text{ K}^{-1}]\))

\[
\begin{align*}
    c_v & \equiv \left( \frac{\partial u}{\partial T} \right)_v \\
    &= \left( \frac{\partial q}{\partial T} \right)_v
\end{align*}
\]

- \( c_v \) : 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 \([J \text{ mol}^{-1} \text{ K}^{-1}]\))

\[
\begin{align*}
    c_p & \equiv \left( \frac{\partial h}{\partial T} \right)_p \\
    &= \left( \frac{\partial q}{\partial T} \right)_p
\end{align*}
\]

- \( c_p \) : 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

\[ h = u + pv = u + R\bar{T} \]

\[ c_p = \left( \frac{\partial h}{\partial T} \right)_p = \left( \frac{\partial (u + \bar{R}T)}{\partial T} \right)_p = c_v + \bar{R} \]
adiabatic expansion of an ideal gas ($c_v = \text{constant}$)

\[
du = \delta q - pv = -pdv
\]

\[
c_v dT = -\frac{RT dv}{v}
\]

\[
c_v \frac{dT}{T} = -\frac{R}{v} dv
\]

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

\[
c_v \ln \frac{T_2}{T_1} = -\frac{R}{v} \ln \frac{v_2}{v_1}
\]

after some math...

\[
pv^\kappa = \text{constant} \quad \text{(with } \kappa = \frac{c_p}{c_v}\text{)}
\]
Adiabatic Expansion

\[ pV^\kappa = \text{constant} \]

\[ \kappa = \frac{c_p}{c_v} \]
**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)

\[ p_1 = p_0 + \rho gh_1 \quad (1) \Leftrightarrow p_0 = p_1 - \rho gh_1 \quad (1a) \]

\[ p_2 = p_0 + \rho gh_2 \quad (2) \Rightarrow p_2 = (p_1 - \rho gh_1) + \rho gh_2 = p_1 - (h_1-h_2)\rho g \quad (2a) \]

Na op druk brengen van de fles volgt adiabatische expansie:

\[ p_1 V_1' = p_2 V_2' \quad (3) \]

Gas na op druk brengen en na de isochore expansie bereikt uiteindelijk dezelfde $T \Rightarrow$

\[ p_1 V_1 = p_2 V_2 \quad (4) \Leftrightarrow \left( \frac{V_1}{V_2} \right)^\gamma = \left( \frac{p_2}{p_1} \right)^\gamma \quad (5) \]

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

\[ \left( \frac{V_1}{V_2} \right)^\gamma = \left( \frac{p_0}{p_1} \right) \quad (6) \]
Clement & Desormes' Experiment (2)

Uit (5) en (6) volgt: \[ \left( \frac{p_2}{p_1} \right)^\gamma = \left( \frac{p_0}{p_1} \right) \quad (7) \]

\[ \gamma = \frac{\ln \left( \frac{p_0}{p_1} \right)}{\ln \left( \frac{p_2}{p_1} \right)} \quad (7a) \]

Verdere vereenvoudiging mogelijk als \( p \) niet te veel van \( p_0 \) afwijkt.

(7) en (1a) \[ \left( \frac{p_1-(h_1-h_2)\rho g}{p_1} \right)^\gamma = \left( \frac{p_1-\rho gh_1}{p_1} \right) \quad (8) \]

\[ \left( 1-\frac{(h_1-h_2)\rho g}{p_1} \right)^\gamma = 1-\left( \frac{\rho gh_1}{p_1} \right) \quad (9) \]

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

\[ 1-\gamma \frac{(h_1-h_2)\rho g}{p_1} = 1-\left( \frac{\rho gh_1}{p_1} \right) \quad \Leftrightarrow \quad \gamma = \frac{h_1}{h_1-h_2} \quad (10) \]