

Chemistry course
ACME Faculty, EHVE course
B.Sc. Studies, I year, I semester
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Thermochemistry and states of matter

How much heat does coal produce?

- Calorific value of coal (power coal) is ca. 22 MJ/kg. What does it mean? Apart from moisture and impurities, if hard coal would consist only of carbon atoms we would have only $C + O_2 \rightarrow CO_2$ reaction (in reality calorific value consist of combustion heat of all atoms/compounds: nitrogen, sulfur, etc.)
- Most of heat from coal combustion comes from that reaction, so it is exothermic (system delivers to surroundings energy by means of heat at expense of its inner energy). Heat of that reaction can be different, though, depending on conditions in which it takes place.
- Estimating heat of reactions is the main subject of interest of thermochemistry.

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Thermodynamic cycle

- In reality, amount of energy released or received during reaction process is calculated by summing up heat of its steps.
- Step is any effect, even imaginary one, as long as its heat is known (most of the simple processes/effects are tabulated).

E.g. reaction $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ can be divided into:
I step: $C_{(s)} \rightarrow C_{(g)}$,
II step: $C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)}$

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Thermodynamic cycle

- Steps, on which reaction is divided, should sum up into initial reaction equation.
- Division on steps requires every step to change any function of state.
- (reminder) Function of state is a quantity depending on state parameters (p, V, T, n_i). Example is inner energy (U) or enthalpy (H). Changes of function of state are independent of pathway of transformation and depend only on initial and final state of a system. Thus, one can divide reaction into any number of steps (in such a way, that heat of each step would be known).

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Functions of state

- thermodynamic potentials

- Here are only four functions of state, also known as **thermodynamic potentials** (two were already presented on previous lectures).
- We cannot calculate or measure absolute values of thermodynamic potentials, but we can measure their changes (we subtract the initial value from the final one). Thus, in reality one can use only changes of those functions:
 - Inner energy (ΔU);
 - Enthalpy (ΔH);
 - Free enthalpy (ΔG) (new one);
 - Free energy (ΔF) (new one).

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Inner energy

$$\Delta U = W + Q$$

(inner energy can only change through heat transfer or work done; work can be volumetric or non-volumetric; in this lecture, unless otherwise noted, there is only volumetric work taken into account – $W = pV$)

For isochoric conditions:

$$\Delta U = Q \quad (V = \text{const})$$

(volumetric work is equal to 0, if volume cannot change), so inner energy change is equal to heat effect (it is how heat effects are measured – in tightly sealed calorimeter chamber).

Usually, reactions are carried out not in isochoric but isobaric conditions (where pressure is constant and is equal to atmospheric one – reaction in unsealed flask case).

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Enthalpy

For isobaric conditions:

$\Delta U = Q - p\Delta V$ ($p = \text{const}$) (if system is giving up energy as work, then ΔV has positive value, so the whole $-p\Delta V$ term is negative – energy is given up to the surroundings and vice-versa)

$$Q = \Delta U + p\Delta V = \Delta U + \Delta(pV) = \Delta(U+pV)$$

$U+pV$ term is called enthalpy.

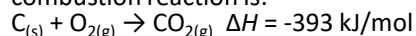
Enthalpy is energy exchanged as heat in isobaric conditions (so the only exchanged energy as work is volumetric work). Thus, it is often called heat effect of reaction (it is the most frequent way of measuring the energetic effect of reaction).

$$H = U + pV \quad Q = \Delta H$$

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Enthalpy

For instance, heat effect of coal combustion reaction is:



(negative value of enthalpy is a result of energy being given up to surroundings, so reaction is exothermic)

Counting coal's average molecular weight

as 12 g/mol (carbon is the main component of coal), one can calculate, that combustion of 1 kg of coal (1000 / 12 = 83.3 mol) will have the heat effect of ca. 32.7 MJ (393 kJ/mol · 83.3 mol = 32737 kJ), which more-less overlaps with calorific value for coal (which contains ca. 80% of pure carbon, 32.7MJ · 0.8 = 26.2 MJ); in reality the calorific value of coal is even lower due to positive enthalpy values for combustion of some coal components, as well as energy needed for evaporation of moisture, for instance)

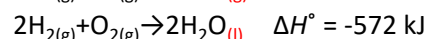
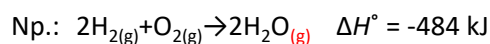
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Enthalpy

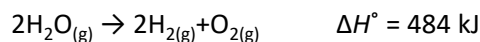
Standard enthalpy of reaction (ΔH°) is the standardized heat effect of the given reaction for the established stoichiometry of reaction equation (often minimal stoichiometric coefficients), 100% reaction yield, standard pressure (1 bar) and standard temperature (25°C), unless reaction cannot occur at room temperature (then it is noted, what temperature does the enthalpy refers to, because enthalpy depends on temperature).

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Enthalpy



Reactions reverse to those above have the same enthalpy, but with the opposite sign:



To decompose water vapor into hydrogen and oxygen lots of energy is needed!

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Enthalpy

- Scheme for calculating heat effect of reaction:

Substrates (reaction mixture before reaction at T,p conditions) $\xrightarrow{\Delta_r H}$ Products (reaction mixture after reaction at T,p conditions)

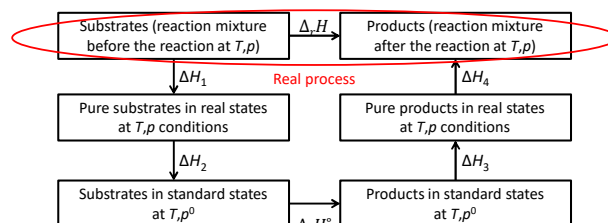
- Unfortunately, such data are almost never tabulated. However, one can derive it using tabulated data:

Substrates (standard state) $\xrightarrow{\Delta_r H^\circ}$ Products (standard state)

- In tables usually one can find enthalpy for standard states and standard conditions. Unfortunately, standard state for water (for instance) is liquid, so for reactions with water vapor, one has to calculate enthalpies for real state (water vapor), and to do the same for product (if the product in reality is not in its standard state). Finally, one has to take into account, that any reaction rarely occurs at room temperature (so reagents have to be heated up – calculated using heat capacities).

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Enthalpy of isothermal process



ΔH_2 i ΔH_3 – heat effects resulting from pressure differences and phase changes for getting reagents from standard state to real state;

ΔH_1 i ΔH_4 – mixing enthalpy (pure reagents vs reaction mixture, solution of few substances in one);

One has to take into account temperature change needed to achieve adequate kinetic conditions to carry out the process (optimal equilibrium) – we'll deal with it together with industrial processes.

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Enthalpy

- If during the reaction in isobaric conditions amount of gaseous reagents changes (different mole quantity of gaseous products and substrates), then one should take into account the volumetric work as well (ca. 2.3 kJ/mole of gaseous reagents difference).

It changes the inner energy of a system.

In case of isochoric reaction (tightly sealed reactor) there is no volumetric work, but all that pressure contribution is counted within enthalpy (pressure increase is causing the heat effect).

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Free enthalpy

- Free enthalpy (G)** – at constant T and p it is the maximal energy exchanged as non-volumetric work (e.g. electrical energy), which can be obtained by transition.
- Free enthalpy is used for chemical reaction and phase transitions (constant temperature – thermostated or achieved by keeping the solvent boiling/reflux, constant pressure – atmospheric for instance, volume can change – unsealed flask is an example of such, entropy is rising, obviously).
- Reaction occurs spontaneously at given T and p , if $G_{\text{substr}} > G_{\text{prod}}$ at those conditions ($dG < 0$).

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Free enthalpy

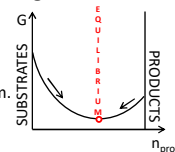
- Free enthalpy criterion of spontaneity is often used for determining of reaction direction (determining point of reaction equilibrium). In other words, if the process occurs spontaneously at given conditions. Any thermodynamic potential can be used for that, though (depending on constraints – which parameters are constant).
- Substrates tend to convert into product to decrease their own energy (aside from entropy increase). In order for reaction to occur, total energy of the system has to decrease.
- ΔG function has its own minimum and that is, where the equilibrium takes place (we know that from the lecture on kinetics). Reaction direction depends on initial state (in which direction does the system needs to go to achieve function minimum).

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Free enthalpy

- Enthalpy of spontaneous reaction at constant T and p conditions will be decreasing until minimum will be achieved – and the reaction will stop (achieve equilibrium).
- From the general condition of spontaneity (entropy increase has to be faster than heat exchange rate $dS \geq dQ/T$):

$$\begin{aligned} dS - (dU - dW)/T &\geq 0 \\ TdS - dU + dW &\geq 0 \quad (\text{for constant } T > 0) \\ TdS - dU + d(pV) &\geq 0 \quad (\text{for non-electrochem.}) \\ TdS - d(U + pV) &\geq 0 \quad (\text{system } W = pV) \\ dH - TdS &\leq 0 \quad (H = U + pV) \\ d(H-TS) &\leq 0 \end{aligned}$$



Free enthalpy is defined as $G = H - TS$ so the spontaneity condition at isothermal-isobaric conditions is $dG \leq 0$ (as long as G can decrease, process is spontaneous and still can occur)

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Free energy

- Free energy (F)** – part of the inner energy, which at constant T and V can be released out of the system as both heat and work (both volumetric and non-volumetric).
- Change of free energy can be easily determined, because it depends on T , V and n . Free energy criterion is used sometimes for reactions that occur at changing conditions or for electrochemical processes.

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Free energy

From the general condition of spontaneity:

$$\begin{aligned} dS - (dU - dW)/T &\geq 0 \\ TdS - dU + dW &\geq 0 \\ d(U-TS) &\leq dW \end{aligned}$$

Free energy is then defined as $F = U - TS$

$$\begin{aligned} dF &\leq dW \\ dF &\leq -pdV \quad (\text{if only volumetric work is considered}) \\ dF &\leq 0 \end{aligned}$$

So the condition of spontaneity of the process at constant T and V is the decrease in free energy.

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Spontaneity of processes

To sum up conditions of spontaneity, depending on constrains:

$$\begin{aligned} V = \text{const}, S = \text{const} & \quad dU \leq 0 \\ S = \text{const}, p = \text{const} & \quad dH \leq 0 \\ p = \text{const}, T = \text{const} & \quad dG \leq 0 \\ T = \text{const}, V = \text{const} & \quad dF \leq 0 \end{aligned}$$

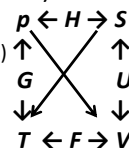
It is possible to make mnemonic scheme for those conditions as well as thermodynamic potentials' formulas.

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Thermodynamic potentials

Thermodynamics mnemonic square (thermodynamic potentials are noted as Y):

On the edges it has thermodynamic constrains in the corners (state parameters) at which those potentials are optimizing functions (for those pairs of constrains spontaneity condition is $dY \leq 0$).



Mnemonics for that square is as follows

(counter-clockwise starting with bottom right corner):

Vice-consul of Uruguay, Secret's Holder Phineas, Got Truckload of Fruits.

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Thermodynamic potentials

Mnemonic square helps with memorization of thermodynamic potentials' total differentials:

$$\begin{aligned} dU &= TdS - pdV & dH &= TdS + Vdp \\ dG &= -SdT + Vdp & dF &= -SdT - pdV \end{aligned}$$

or partial derivatives of those potentials:

$$\begin{aligned} (\partial U / \partial V)_S &= -p & (\partial U / \partial S)_V &= T & p &\leftarrow H \rightarrow S \\ (\partial H / \partial S)_p &= T & (\partial H / \partial p)_S &= V & \uparrow & & \uparrow \\ (\partial G / \partial p)_T &= V & (\partial G / \partial T)_p &= -S & G & & U \\ (\partial F / \partial T)_V &= -S & (\partial F / \partial V)_T &= -p & \downarrow & & \downarrow \\ & & & & T &\leftarrow F \rightarrow V \end{aligned}$$

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Spontaneity vs reaction rate

Spontaneity and reaction/process direction can be determined basing on initial conditions and by knowing heat effects of reaction.

Thermodynamics are not kinetics, though.

Thermodynamic data can only determine "if", not "how fast" (that is the subject of kinetics).

In reality it can happen, that thermodynamically spontaneous reaction does not occur, *i.e.* it occurs, but too slow for any practical application.

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Metastable states

- Steady state, which is not changing (in practical terms) due to too small process rate (due to being in local energy minimum) is **metastable state**.
- Diamonds are popular example (as well as few other minerals), which were formed under extremely high pressure and temperature. In standard conditions (T, p) graphite is the stable form of carbon and diamonds are metastable. Diamond-graphite transition at room conditions would take billions of years. However, in high temperatures rate of this transition can be much higher.

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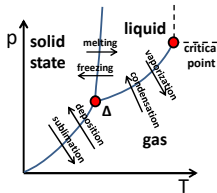
Metastable states

- Other example of metastability is supercooled/superheated liquid. For crystallization or boiling (*e.g.* water) stimulus is needed for bubble/crystal nucleation.
- Role of such stimulus is usually taken by impurity or other non-ideality (*e.g.* irregularity of vessel surface, vibrations, *etc.*). If there would be very pure liquid (redistilled, for instance) in a vessel with very smooth surfaces (in microscopic terms) and temperature would be changed very slowly (avoiding any vibrations, non-uniform heat propagation – *e.g.* using microwaves, *etc.*), one can obtain liquid water below 0°C or above 100°C .

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Phase transition

- Phase transition is change of state. There are three state of matter boundaries (liquid-gas, gas-solid, solid-gas) and six phase transitions (vaporization, condensation, melting, freezing, sublimation and deposition).



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Phase transition

- At boundaries that separates **phase stability fields** substance is in two phases that co-exist (in case of boiling water it means that water vapor in form of bubbles co-exist with liquid water).
- In **phase diagram** two points are notable: triple point and critical point.
- Triple point (Δ)** is when all three phases co-exist at the same conditions.

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Phase transition

- Critical point** is the point, above which there can be no distinction between liquid and gas. Such state is called a **fluid** (apart from that meaning, fluid in engineering is every substance that can flow – gases, liquids, emulsions and so on).
- Fluids have variable density (depending on pressure), do not have meniscus and fill out all available space (like gas). Critical point of water takes place at $T = 647 \text{ K}$ (374°C) and $p = 221 \text{ bar}$.

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Phase transition

- First order phase transition** (melting, vaporization, sublimation, etc.) is characterized by discontinuity of parameters such as volume, heat capacity, entropy, enthalpy (derivatives of free enthalpy G), etc. In practice it means that water at 100°C has completely different heat capacity than water vapor at 100°C (ca. two-fold difference; we neglect here heat capacity dependence of temperature, which is about 2% every 100°C).

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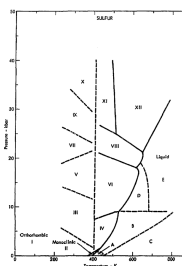
Phase transition

- There are also **second order phase transitions**, which do have continuity of all of those parameters, apart from heat capacity (second derivative of free enthalpy). A good example of such phase transition is superconducting phase transition and glass transition.

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Phase transition

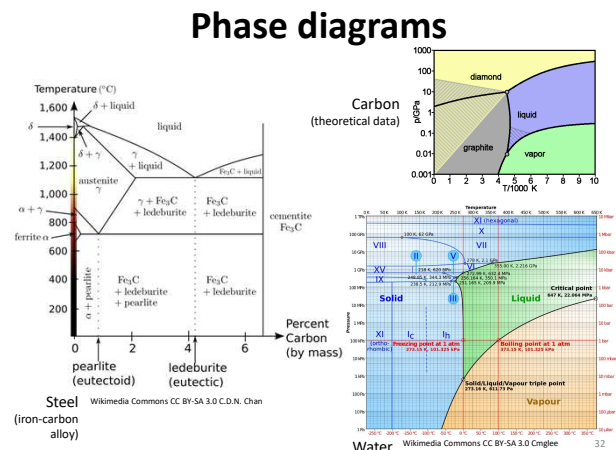
- Other type of first order phase transition is allotropic transition (polymorphic), *i.e.* particular allotropic forms of element (substance) are stable in different parts of T,p chart.
- Co-existence of few different forms at the same conditions can be a result of wide ranges of metastability around the stable fields for a particular form (in a given conditions range only one form can be thermodynamically stable, but at a given point even few metastable and one stable range can overlap; after forming in a stable conditions range, material can be stored in other conditions, in which it is metastable).



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Phase diagrams

- Apart from phase diagrams for pure substances (elements, compounds) there are also phase diagrams of mixtures (or alloys), where one additional axis is used for content (fraction of one of components).
- Due to difficulty of reading and drawing multidimensional diagrams (especially those above 3D) usually two most important parameters are used for axis and the third one is constant (or a series of diagrams is drawn with every at a different third parameter value). If there are more components, one can use ternary plot or isometric projection of 3D diagram.



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Evaporation

Every liquid has its vapors above its surface (meniscus). At a given temperature it will tend to a constant vapor pressure value (pressure of one of gaseous components is called **partial pressure**, pressures are additive and their sum is equal to gas mixture pressure – like air pressure is sum of partial pressure of oxygen and nitrogen) – it is called **saturated vapor pressure**. Of course, in order to achieve such pressure constant volume is needed. If one has a glass of water left on the air, then air movement (wind) is blowing water vapor of from above the water meniscus. Thus, water is not able to achieve saturated vapor pressure, so it is vaporizing all the time, until eventually it would vaporize completely. However, if water is kept in a closed bottle, water will achieve vapor pressure in a given temperature and will stop vaporizing.

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Boiling

Boiling is taking place when atmospheric pressure is lower than liquid's vapor pressure in the given temperature. It is possible to achieve by increasing temperature (vapor pressure is increasing with temperature) until vapor pressure will exceed atmospheric pressure (in case of water vapor pressure at $T = 100^\circ\text{C}$ is $p_{\text{H}_2\text{O}} = 1000 \text{ hPa}$).

Other method is to decrease pressure (in high mountains pressure of atmosphere is reduced, so water boils at lower temperature), which is used in vacuum ovens. Of course, both methods can be mixed.

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Boiling

- Decreasing pressure and increasing temperature is a basis for **vacuum oven** operation (using **rotary pump** $p < 10 \text{ Pa}$) and for rotary **vacuum evaporator** (using **water aspirator** $p = 2000 \text{ Pa}$).
- Thanks to it, it is possible to dry materials (separate liquid from solid) without use of high temperature (not to decompose or melt solid substance).
- To estimate boiling point drop due to reduced pressure, Trouton's rule become in handy.

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Trouton's rule

- Formula for calculating liquid's boiling point at the given pressure:
$$T = T_b \frac{X}{X - \ln\left(\frac{p}{p_{\text{atm}}}\right)}$$
- Formula for calculating saturated vapor pressure at the given temperature:
$$\ln\left(\frac{p}{p_{\text{atm}}}\right) = -X \left(\frac{T_b - T}{T}\right)$$

p_{atm} – atmospheric pressure (101325 Pa);

T_b – boiling point of liquid at p_{atm} ;

T – given/calculated temperature; p – given/calculated pressure;

X – coefficient ($\Delta_p S/R$) resulting from Trouton's rule.

- Trouton's rule states that for most of liquids X is equal to 10.3 (one of the few exceptions is water: 13.1; also methanol: 12.6; acetic acid: 7.4).

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Trouton's rule

I example: To what temperature boiling point of water will drop at 2000 Pa pressure (achievable by water aspirator)?

$$T = T_b \cdot X / (X - \ln(P/P_{\text{atm}})) = 373 \cdot 13.1 / (13.1 - \ln(2/101)) = 373 \cdot 13.1 / (13.1 + 3.9) = 373 \cdot 0.77 = 287 \text{ [K] (ca. } 14^\circ\text{C)}$$

II example: Solution of ABC compound in cyclohexane is given (filtrate after post-reaction purification). ABC compound is instable at temperatures above 50°C. What minimum pressure has to be maintained in order to dry ABC from cyclohexane (evaporate cyclohexane) and to keep save margin?

$$T = 40^\circ\text{C} = 313 \text{ K}, T_{b(\text{cyclohexane})} = 81^\circ\text{C} = 354 \text{ K?}$$

$$\ln(P/P_{\text{atm}}) = -10.3 \cdot (354 - 313) / 313 = -10.3 \cdot 0.13 = -1.35$$

$$p/p_{\text{atm}} = \exp(-1.35) = 0.259 \quad p \approx 25900 \text{ Pa} = \mathbf{259 \text{ mbar}}$$

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Compression of solid bodies and liquids

Phase diagrams are showing effects of solids compression. Such effect is much less visible than in case of gases, it is measurable, though. There are three thermoelastic coefficients:

- **Isobaric thermal expansion coefficient (α)** (most popular of those three due to practical applications in construction engineering, putting up overhead power lines and railway electric traction)

$$\alpha(T - T_0) = \ln(V/V_0) ;$$

- **Isothermal compression modulus of elasticity (κ)**

$$\kappa(p - p_0) = -\ln(V/V_0) ;$$

- **Isochoric thermal pressure coefficient (β)**

$$\beta = \alpha / \kappa .$$

$$(T_0 - \text{temperature} = 25^\circ\text{C}; p_0 - \text{atmospheric pressure} = 1 \text{ atm})$$

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Compression of solid bodies and liquids

Data for copper (power lines – when designing, it is needed to consider expansion and compression with some margin):

$$\alpha = 5.0 \cdot 10^{-5} \text{ K}^{-1} \quad \kappa = 7.8 \cdot 10^{-12} \text{ Pa}^{-1}$$

Data for mercury (old thermometers, thermal expansion coefficient is almost independent from temperature, so it can be used in wide range for temperature measurements):

$$\alpha = 1.3 \cdot 10^{-4} \text{ K}^{-1} \quad \kappa = 3.8 \cdot 10^{-11} \text{ Pa}^{-1}$$

Data for water:

$$\alpha = 2.1 \cdot 10^{-4} \text{ K}^{-1} \quad \kappa = 4.9 \cdot 10^{-10} \text{ Pa}^{-1}$$

Other consequences of expansion/compression: in case of objects designed to endure thermal shock their construction materials should be chosen in terms of the lowest α (e.g. oven ware). Also, sealed containers containing liquids need to have some margin/safety valve (e.g. batteries).

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