GLOSSARY
THERMODYNAMICS

work (w, J) is the scalar product of the applied force and the displacement of the object (in the direction of force).

energy (E, J) is the capacity to do work or to produce change.

heat (q, J) is an energy transfer induced by temperature difference.

endothermic process is a process where heat is absorbed from the surroundings.

exothermic process is a process where heat is released to the surroundings.

internal energy (U, J) is the total energy of the system. It contains the translational, rotational, vibrational, electronic, and nuclear energies and the energies due to intermolecular interactions. Its absolute value is unknown, its change is defined by the first law of thermodynamics. It is a state function and an extensive quantity.

state function is a property that is determined by the state of the system. The change in the state function is path independent and defined by the properties in the initial and the final state only.

Zeroth law of thermodynamics states that if system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system C is also in thermal equilibrium with system A ($T_A = T_B = T_C$).

First law of thermodynamics states that in closed system the internal energy can be changed by work or heat only, i.e., $\Delta U = q + w$.

reversible process is a process in which the system is always infinitesimally close to equilibrium. Such a process can never be observed, it is only of theoretical interest.

enthalpy (H, J) H=U+pV, where U is the internal energy, p pressure and V volume. Its change gives the heat at constant pressure when there is no other work.

heat capacity (C, J/K) at constant volume: $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$ and at constant pressure: $C_p = \left(\dfrac{\partial H}{\partial T}\right)_p$ where U denotes the internal energy, T the temperature, and H the enthalpy.

enthalpy of reaction is the change in the enthalpy during a reaction.

standard molar enthalpy of formation The enthalpy change when 1 mole of a compound is synthesized from its elements in their standard states of one bar at some temperature.

Hess' law states that the change in the enthalpy of a reaction is the sum of the enthalpies of reactions from which the reaction can be built.

Second law of thermodynamics states that in isolated systems the entropy increases in spontaneous processes, i.e., $\Delta S > 0$; in reversible process at equilibrium it is constant, i.e., $\Delta S = 0$. *or* It is impossible to convert heat completely into work. *or* Heat cannot spontaneously flow from a material at lower temperature to a material at higher temperature.

entropy (S, J/K) is a thermodynamic quantity that expresses the degree of disorder or randomness in a system at the molecular level $dS = \delta q_{rev}/T$.

Third law of thermodynamics states that every substance has finite positive entropy except the entropy of pure, perfect crystalline structure wich is 0 at 0 K.

Helmholtz energy (A, J) defined as A=U-TS, where U is the internal energy, T is the thermodynamic temperature and S is the entropy. The change in Helmholtz energy at constant volume and temperature gives the maximal work available. In a closed system at constant volume and temperature the Helmholtz energy decreases during a spontaneous process.

Gibbs energy (G, J) defined as G=H-TS, where H denotes enthalpy, T the thermodynamic temperature and S the entropy. The change in Gibbs energy at constant pressure and temperature gives the maximal work available. In a closed system at constant pressure and temperature the Gibbs energy decreases during a spontaneous process.

Carnot or thermodynamic efficiency (η)

$$\eta = \frac{|w_{max}|}{|q_m|} = 1 - \frac{T_h}{T_m},$$

where T_h denotes the lower temperature while T_m the higher one.

coefficient of cooling performance (c)

$$c = \frac{\text{heat extracted from the cold system}}{\text{work done on the system}} = \frac{|q_h|}{|w|}$$

maximum value of the coefficient of cooling performance (c_{max})

$$c_{max} = \frac{|q_h|}{|q_m| - |q_h|} = \frac{T_h}{T_m - T_h} ,$$

where T_h denotes the lower temperature while T_m the higher one.

chemical potential partial molar Gibbs energy which can be written for the ith component $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j \ j\neq i}$

Gibbs-Duhem's equation $\sum\limits_{i=1}^{C} n_i d\mu_i = 0$, where C denotes the number of components.

Phase rule F=C-P+2, where F denotes the degrees of freedom, C the number of components, while P the number of phases.

(thermodynamical) degree of freedom (for the system) is the number of intensive variables that can be changed independently in the system without disturbing the number of phases in equilibrium.

chemical potential for ideal gases $\mu = \mu^0 + RT \ln (p/p^0)$, where μ^0 is the standard chemical potential.

chemical potential for nonideal gases $\mu = \mu^0 + RT \ln (f/p^0)$ where $f = \gamma p$ is the fugacity of the gas, γ the fugacity coefficient and μ^0 the standard chemical potential (hypothetical state where $f = p^0$ and the gas behaves ideally).

Clapeyron's equation $\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$, where ΔS_m and ΔV_m represent the changes in molar entropy and volume during the appropriate phase change.

Clausius-Clapeyron's equation

$$\frac{d(\ln p)}{dT} = \frac{\Delta H_m}{RT^2} , \quad \text{in integrated form:} \quad \ln\frac{p_2}{p_1} = \frac{\Delta H_m}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where ΔH_m represents the change in molar enthalpy during the appropriate phase change between phases 1 and 2.

Gibbs energy of mixing for ideal mixtures $\Delta_{mix}G = nRT \sum_{i=1}^{C} x_i \ln x_i$, where n is the total amount of substance, C the number of components, and x_i is the mole fraction of the ith component in the mixture.

entropy of mixing for ideal mixture $\Delta_{mix}S = -nR \sum_{i=1}^{C} x_i \ln x_i$, where n is the total amount of substance, C the number of components, and x_i is the mole fraction of the ith component in the mixture.

ideal solution is a solution in which both the solvent and the solute obey Raoult's law for any composition (since $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$).

Raoult's law for any component $p_i = x_i p_i^*$, where p_i is the vapor pressure of the component and p_i^* is the vapor pressure of the pure component and x_i is the mole fraction of the component in the solution.

Henry's law is $p_{solute} = K_H x_{solute}$, where p is the partial pressure of the gas above the solution, K_H the Henry's constant and x_{solute} is the mole fraction of the solute in the solution.

ideal dilute solution a solution in which the solvent obeys Raoult's law and the solute obeys Henry's law.

activity $\mu_i = \mu_i^* + RT \ln a_i$, where a_i is the activity of the ith compound and μ_i^* the chemical potential which is that of the pure solvent for the solvent ($a = p/p^*$), while that of the solute in an infinitely dilute solution for the solute ($a = p/K_H$).

activity coefficient $a_i = \gamma_i x_i$, where γ_i is the activity coefficient of the ith compound.

electrolyte is a compound which in its liquid form behaves as an electrically conducting medium.

mean ionic activity $a_\pm = \left(a_+^{\nu_+} \cdot a_-^{\nu_-} \right)^{1/\nu}$, where $\nu = \nu_+ + \nu_-$.

ionic strength $I = 1/2 \sum_{i=1}^{C} c_i z_i^2$, where C is the number of ions, c the concentration of ions while z is their charges.

Debye-Hückel limiting law $\lg \gamma_\pm = -0.509 |z_+ z_-| \sqrt{I/(\text{mol dm}^{-3})}$, where $\gamma_\pm$ is the mean ionic activity coefficient.

molarity or molar concentration (c, mol/dm^3) $c_B = n_B/V_{solution}$, where n_B denotes the amount of substance of the solute and $V_{solution}$ the volume of the solution.

molality ($\bar{m}$, mol/kg) is the amount of substance of the solute (n_B) divided by the mass of the solvent m_A, i.e., $\bar{m}_B = n_B/m_A$.

colligative properties are properties independent of the nature of the compounds and depend on the numbers of the solute particles only. e.g. osmosis, boiling point elevation, freezing point depression, vapor pressure lowering

osmosis movement of the solvent through a semipermeable membrane from a dilute solution to a more concentrated one.

osmotic pressure $\pi = c_{solute}RT$, where c_{solute} is the concentration of the solute. The pressure can be determined by measuring height difference at the two end of the membrane: $\pi = \rho gh$, where h is the height difference, g is the acceleration constant.

freezing point depression $\Delta T_f = \Delta T_{M,f} \bar{m}_B$, where $\Delta T_{M,f}$=1.86 K kg/mol is for aqueous solution.

boiling point elevation $\Delta T_b = \Delta T_{M,b} \bar{m}_B$, where $\Delta T_{M,b}$=0.52 K kg/mol is for aqueous solution.

partition is the dissolution of a substance in two immiscible liquids.

Nernst partition law $\dfrac{c_{X,A}}{c_{X,B}} = K_{m,c}$ where $c_{X,A}$ denotes the concentration of X dissolved in A, while $c_{X,w}$ that in B.

Octanol water partition coefficient $K_{o/w} = \dfrac{c_{X,o}}{c_{X,w}}$, where $c_{X,o}$ denotes the concentration of X in octanol, while $c_{X,w}$ that in water.

reaction coordinate $\xi = (n_i - n_i^0)/\nu_i$, where n_i the amount of substance of the ith compound, n_i^0 the initial amount of substance and ν_i its stoichiometric coefficient.

LeChatelier's principle states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way to decrease the effect of the stress.

equilibrium constant $K_a = \dfrac{a_K^k \cdot a_L^l \cdot a_M^m \cdots}{a_A^a \cdot a_B^b \cdot a_C^c \cdots} = \dfrac{(c_K\gamma_K)^k \cdot (c_L\gamma_L)^l \cdot (c_M\gamma_M)^m \cdots}{(c_A\gamma_A)^a \cdot (c_B\gamma_B)^b \cdot (c_C\gamma_C)^c \cdots} = K_c K_\gamma$

determination of equilibrium constant from the Gibbs energy $\Delta_r G^0 = -RT \ln K_a$, from which $K_a = e^{-\Delta_r G^0/(RT)}$

calculation of $\Delta_r G^0$ $\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$

REACTION KINETICS

reaction rate $v = (1/v_j)\, dc_j/dt$, where v_j is the stoichiometric coefficient of the jth component.

empirical rate law $v = k \prod_{i=1}^{r} c_i^{\beta_i}$ where v is the reaction rate, k the rate constant, while β_i is the reaction order with respect to component i.

rate constant is a constant of proportionality between the reaction rate and the concentrations of reactants.

reaction order with respect a component is the power to which the concentration of the component is raised.

reaction order sum of all powers appearing in the empirical rate law.

half life is the time required for the concentration of a reactant to decrease to half of its initial concentration.

rate law for a first-order reaction $v = -d[A]/dt = k[A]$, where [A] represents the concentration of the reactant.

integrated rate law for a first-order reaction

$$[A] = [A]_0 e^{-kt} \quad \text{or} \quad \ln\frac{[A]}{[A]_0} = -kt\,,$$

where $[A]_0$ denotes the initial concentration of the reactant, [A] the reactant concentration corresponding to time t, and k the rate constant.

half life for a first-order reaction $t_{1/2} = \ln2/k$, where k is the rate constant.

Arrhenius eqation $k = A\exp(-E_A/RT)$ or in linearized form $\ln k = \ln A - E_A/RT$, where A denotes pre-exponential factor, E_A the activation energy, and T the temperature.

elementary step is a reaction step that represents the reaction at the molecular level.

reaction mechanism is the sequence of elementary steps describing the time evolution of the system.

catalyst is a substance that increases the rate of a reaction without itself being consumed.

catalysis is a process carried out with the help of a catalyst.

autocatalyst is a catalyst which is one of the products of the reaction, i.e., the product accelerates its own production.

autocatalysis is a process carried out with the help of an autocatalyst.

parallel reactions are reactions taking place at the same time.

consecutive reactions are reactions taking place in sequence, i.e., the product in one system may be a reactant in the other.

steady-state approximation $dc_i/dt \approx 0$ assumes that the concentration of a reaction intermediates is constant during the main part of the reaction. The approximation is not valid around the initial time.

Michaelis-Menten equation

$$v = \frac{v_{max}[S]}{[S] + K_M},$$

where v denotes the rate of formation, v_{max} is the maximum rate of formation, and K_M the Michaelis constant.

Lineweaver-Burk plot is 1/v - 1/[S] function yielding a linear dependence. From the slopes and the intercepts K_M and v_{max} can be determined.

$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_M}{v_{max}} \frac{1}{[S]}$$

chain reaction is a group of reactions where chain carriers are produced which by further reacting with the reactant produce back the chain carriers.

chain carrier is an intermediate responsible for the propagation of a chain.

initiation step is a reaction step where the first chain carriers are formed.

propagatin step is a reaction in which the number of chain carriers is constant.

branching step is a reaction in which the number of chain carriers increases.

retardation step is a reaction where the number of chain carriers is constant but the product is consumed.

termination step is a reaction in which the number of chain carriers decreases.

SPECTROSCOPY AND PHOTOCHEMISTRY

spectroscopy is the study of the interaction between electromagnetic radiation and matter.

photochemistry is the study of the absorption of radiation and the reactions of excited particles.

Lambert-Beer law $A = \lg(I_0/I_T) = \varepsilon cl$, where A denotes absorbance, I_0 intensity of incident light, I_T intensity of transmitted light, ε molar absorbance, l pathlength.

fluorescence is the emission of electromagnetic radiation by a substance in singlet state while the substance is illuminated. The process can be described by first-order kinetics.

phosphorescence is the emission of electromagnetic radiation by a substance in triplet state while the substance is illuminated. The process can be described by first-order kinetics.

intersystem crossing is a radiationless transition of a molecule from one electronic state into another one with different spin multiplicity.

internal conversion is a radiationless transition of a molecule from one electronic state into another one with the same spin multiplicity.

quantum yield (ϕ)

$$\Phi = \frac{\text{number of molecules produced}}{\text{number of photons absorbed}}$$

$$\Phi = \frac{\text{rate of process}}{\text{number of photons absorbed in unit time and volume}}$$

chromophore is a part of a molecule that absorbs light of a specific wavelength.

SURFACE REACTIONS

adsorption is the accumulation of particles at a surface.

absorption is a process during which molecules enter the bulk phase of the substance.

desorption is a process where a substance is released from the surface.

adsorbate is te substance that adsorbs.

adsorbent is the substance which is adsorbed.

physisorption is a process where the interaction between adsorbate and substrate is van der Waals type.

chemisorption is a process where the interaction between adsorbate and substrate is a chemical bond.

fractional coverage, (θ)

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$$

adsorption isotherm is the fractional coverage as a function of pressure at constant temperature.

Langmuir isotherm

$$\theta = \frac{Kp}{1 + Kp},$$

where K is the ratio of the rate coefficient of adsorption and desorption.

TRANSPORT PROCESSES

transport process is the flow of matter, energy or momentum from one place to the other.

flux (J) is the amount of the property passing through unit area per unit time.

diffusion is the movement of substance induced by concentration gradient.

Fick's first law $J_d = -D\frac{dc}{dz}$, where D denotes the diffusion coefficient, c the concentration and z is the direction of flow.

convection is the flow of heat or matter by the macroscopic movement of the fluid.

migration is the movement of ions induced by the external electric potential applied.

convective flux (J_k, $\mathrm{mol\,m^{-2}s^{-1}}$) is the amount of substance flown through unit area per unit time due to convection. $J_c = cv_z$, where c denotes concentration and v_z the velocity of the fluid flow in the direction of the flow.

heat flux (J_h, $\mathrm{J\,m^{-2}s^{-1}}$) is the energy flown through unit area per unit time due to heat conduction. $J_h = -\lambda\frac{dT}{dz}$, where λ denotes heat conductance, T temperature and z the direction of the flow.

flux of the momentum (J_i, $\mathrm{kg\,m^{-1}s^{-2}}$) is the momentum flown through unit area per unit time with $J_i = -\eta\frac{dv_x}{dz}$, where η denotes viscosity, v_x is the velocity in the direction of flow and z the direction perpendicular to that.

Fick's second law

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2},$$

where c denotes concentration, z the direction of propagation and, D diffusion coefficient.