Chemical Potential in Focus – Flow of Substances and its Consequences

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Outline

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2. Influence of the Milieu
3. Flow of Substances and Indirect Mass Action
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1. Introduction – Chemical Potential
Introduction

The benefit of chemical thermodynamics is beyond question but the field is reputed to be difficult to learn. One of its most important fundamental quantities, the chemical potential $\mu$, commonly defined as the partial derivative

$$\mu = \left( \frac{\partial G}{\partial n} \right)_{p,T}$$

of a quantity which involves energy and entropy, seems especially hard to grasp.
Chemical Potential as Basic Concept

However, there is a simpler and faster way to an understanding of this quantity that does not make use of higher mathematics.

\[ \mu = \left( \frac{\partial G}{\partial n} \right)_{\rho,T} \]

We propose to introduce \( \mu \) as “tendency to transform” which is firstly characterized by its typical and easily observable properties, i.e. by designing a kind of “wanted poster” for this quantity.

The phenomenological definition is followed by a direct measuring procedure, a method usual for various basic quantities such as length, time and mass.
The strength of this tendency, meaning the numerical value of $\mu$, is determined by the nature of the substance, as well as by its milieu (temperature, pressure, concentration, ...), but not by the nature of reaction partners or the products.

A reaction, transition, redistribution can only proceed spontaneously if the tendency for the process is more pronounced in the initial state than in the final state, i.e. it exists a potential drop:

$$\sum_{\text{initial}} \mu_i > \sum_{\text{final}} \mu_j.$$
The proposed approach is elementary, does not require any special previous knowledge and immediately leads to results which can be utilized practically. This allows to start teaching the subject even at introductory high school level.

Selected illustrative but nevertheless simple and safe demonstration experiments contribute essentially to deepen the comprehension and forge links with everyday experiences.
2. Influence of the Milieu
Temperature and Pressure Dependence

As mentioned the numerical value of the chemical potential $\mu$
- is not only determined by the *nature* of the substance, but also
- by its *milieu* (temperature, pressure, concentration, ...).

Therefore, a more detailed approach has to consider the temperature and pressure dependence of $\mu$. Often linear approximations are sufficient:

$$\mu = \mu_0 + \alpha \cdot (T - T_0)$$
$$\mu = \mu_0 + \beta \cdot (p - p_0)$$

$\mu_0$ : initial value

The *temperature coefficient* $\alpha$ of the chemical potential is (nearly) always negative whereas the *pressure coefficient* $\beta$ is (nearly) always positive.
Mass Action

The tendency $\mu$ of substances to transform depends also on their amounts $n$ or more precisely, their concentrations $c (= n/V)$.

Not the mass of a substance is decisive for mass action, but its “massing”, its “density” in a space, i.e. not the amount, but the concentration.

The more concentrated the application the more intense the effect.

Example: *Evaporation* of water

$$H_2O|l \rightarrow H_2O|g$$

$\mu^0/kG \quad -237 < -229 \quad [G(\text{ibbs}) = J \text{ mol}^{-1}]$

However, if the water vapor is diluted by air, the value of its chemical potential decreases below that of liquid water.
Concentration Dependence I

If the concentration change $\Delta c = c - c_0$ is small, again a linear approach can be chosen:

$$\mu = \mu_0 + \gamma \cdot (c - c_0)$$

While $\alpha$ and $\beta$ (except for gases) still depend from the type and the milieu of the given substance the concentration coefficient $\gamma$ is a universal quantity, i.e. it is the same for all substances in every milieu:

$$\gamma = \frac{RT}{c} \text{ for small } c \text{ at constant } T$$

The combination of these two relations results in the so-called “mass action equation”:

$$\mu = \mu_0 + RT \ln(c/c_0) = \mu_0 + RT \ln c_r$$
Concentration Dependence II

If the concentration $c$ decreases one decade (a factor of ten), the chemical potential always decreases by the same amount, the “deca potential” $\mu_d$ (5.71 kG $\approx$ 6 kG at 298 K).

2. Influence of the Milieu

The basic value $\mu^\circ$ of the chemical potential of the dissolved substance (i.e. the value for the standard concentration $c^\Theta = 1 \text{ kmol m}^{-3}$) coincides with the logarithmic approximation and not with the measured function!

If the concentration $c$ decreases one decade (a factor of ten), the chemical potential always decreases by the same amount, the “deca potential” $\mu_d$ (5.71 kG $\approx$ 6 kG at 298 K).
3. Flow of Substances and Indirect Mass action
Flow of Substances

tendency to spread out in space easily noticeable in the case of strong smelling or colored substances e.g. scent of perfume or pungent odor of potent cheese

migration of a substance B considered as transformation:

\[
\text{B|Origin} \rightarrow \text{B|Destination}
\]

⇒ transport of substances always in direction of a potential gradient, principally caused by the concentration dependency of \( \mu \):

substance migrates from regions of higher concentration (\( \mu \) high) into regions of lower concentration (\( \mu \) low)

⇒ phenomenon of \textit{diffusion}
Indirect Mass Action I

formulation of the mass action equation with the aid of mole fraction $x$:

$$\mu = \mu_0 + RT \ln(x/x_0) \quad x, x_0 \ll 1$$

special case: $x_0 = 1 \Rightarrow$

$$\mu = \dot{\mu} + RT \ln x \quad \text{for } x \to 1$$

with $\dot{\mu}$ as basic value, which corresponds in this case to the chemical potential of the pure substance

solid curve: ideal logarithmic relation

shape of curve near the point $x = 1$: all the $\mu(x)$ curves exhibit the same slope $RT$
Indirect Mass Action II

chemical potential of substance A after addition of a small amount of foreign substance B:

\[ \mu_A = \mu_A + RT \ln x_A = \mu_A + RT \ln(1 - x_B) \quad \text{for } x_A \to 1 \]

diluted solution: \( \ln(1 - x_B) = -x_B \)

\[ \mu_A = \mu_A - RT \cdot x_B \quad \text{indirect mass action equation} \]

\( \Rightarrow \) universal law, independent of the type of substance in question

resulting experimentally observable effects like

- development of osmotic pressure
- freezing-point depression of the solution

only depend from the mole fraction \( x_B \) und therefore the number of dissolved particles and not from their chemical nature (colligative properties)
4. Osmosis
Osmosis

two solutions with different concentrations of a substance B are separated by a wall that only allows solvent A to pass through (so-called semipermeable membrane)
migration of solvent A according to the potential drop

\[ A(\text{pure}) \rightarrow A(\text{diluted with B}) \]

biological membranes surrounding living cells are also semipermeable

⇒ juice is “drawn out” from sugared fruit, cherries burst after a long rain
Juice “Extraction” from Slices of Salted Radish

Procedure:
Unsalted and salted slices of white radish are speared on a meat skewer.

Observation:
Immediately, juice begins to drip out of the stack with the salted slices.

Explanation:
The solvent water migrates from the more diluted solution within the cells of the radish through the semipermeable cell membrane into the concentrated, therefore water-poor, salt solution on the outside.
4. Osmosis

**Osmotic Cell**

Potential drop of solvent A:

\[ \mu_A = \dot{\mu}_A - RT \cdot x_B \]

for \( x_B << 1 \)

Suppression of inflow of solvent by increasing the pressure on the solution

\[ \Rightarrow \text{osmotic equilibrium} \]

\[ \dot{\mu}_A - RT \cdot x_B + \beta \cdot \Delta p = \dot{\mu}_A \]

\[ p_{\text{osm}} = \Delta p = \frac{RT}{\beta} x_B \quad \text{osmotic pressure} \]

\( x_B = n_B/(n_A + n_B) \approx n_B/n_A \) (because \( n_B << n_A \) in a diluted solution) and \( \beta = V_m = V/n_A \):

\[ p_{\text{osm}} = n_B \frac{RT}{V} \quad \text{VAN'T HOFF} \]

\[ \Rightarrow \text{great similarity to general gas law} \]
Osmotic Cell

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Procedure:
A colored saturated CaCl₂ solution is filled into the hollowed carrot and a riser pipe is attached.

Observation:
After a short time, one observes a continuous rise of the solution in the riser pipe.

Explanation:
The solution in the cavity is more strongly concentrated and the solvent therefore more diluted than in the cells of the carrot. Because of the corresponding potential drop solvent flows through the semipermeable cell membrane into the salt solution. As result the liquid begins to rise in the riser pipe.
5. Outlook
5. Outlook

Outlook

- temperature and pressure dependence
- mass action
- related energy exchange
- mixtures
- transport phenomena
- indirect mass action
- prediction of reactions
- quantum statistics
- spectroscopy and photochemistry
- electrochemical cells
- ionic interaction
- redox systems
- reaction kinetics
- heat effects
- interfacial phenomena
Thank you very much for your friendly attention.

Further informations (lecture notes, descriptions of experiments, videos etc.):

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