A quote of the week
(or camel of the week):

It is amazing what you can accomplish if you do not care who gets the credit.

Harry S Truman
Dissolution of gases in liquids. Henry’s law.

It was found empirically, that, \( w = k \cdot P \), or amount of gas dissolved in liquid is, under isothermal conditions, directly proportional to its pressure.

If the gas is the perfect gas, then:
\[
  \begin{align*}
  w &= M \cdot n = M \cdot \frac{PV}{RT} \\
  V &= \frac{wRT}{MP} = \frac{kRT}{M} = \text{const.}
  \end{align*}
\]

and, at \( T=\text{const.} \):

There are also true, Henry’s laws for different concentrations:
\[
  \begin{align*}
  m &= k_m \cdot P \\
  c &= k_c \cdot P \\
  x &= k_x \cdot P
  \end{align*}
\]

200 years of Henry’s law (1803) !!!

In a two component system (liquid + gas), at \( T=\text{const.} \), 1 degree of freedom exists, then pressure defines the state of the system unambiguously. Pressure of liquid vapour is usually small as compared with gas pressure. Therefore, Gibbs’s phase rule alone substantiate the claim, that solubility of gases in liquids is function of pressure at constant temperature.

The bottom formulations of Henry’s law are true, because \( m, c \) and \( x \) are proportional in diluted solutions.
**Henry’s law (2)**

In this form Henry’s law is a limiting law (small concentrations) practically for any dissolved substance B:

\[ x_B = k_{xB} \cdot P_B \]
\[ m_B = k_{mB} \cdot P_B \]
\[ c_B = k_{cB} \cdot P_B \]

From Henry’s law (for gases) it is true, that: \[ \frac{dc}{c} = k dP \]

Hence, Cl.-Cl. Equation must be true:

\[ \frac{d \ln c}{dT} = \frac{\Delta H_{rop}}{RT^2} \]

Salt effect (in water) is described by the following:

\[ \log \frac{S_0}{S} = k \cdot c \]

First conclusion is obvious if we notice that at low pressures, total pressure is not almost exclusively that of pressure of component B, \( P_B \), but some of both. Molar fraction in liquid must therefore proportional to the partial pressure of this component. This is true even for gases

Solubility for gases is influenced by their nature (ability to interact with water, even up to chemical reaction – \( \text{CO}_2, \text{NH}_3 \)), temperature and contents of electrolytes in the solvent. \( S_0 \) – solubility in pure water, \( S \) – solubility in the solution of concentration \( c \), \( k \) – constant, specific for electrolyte, gas independent.
Definitions of partial molar volumes and Gibbs–Duhem equation were discussed in lecture 5 (previous semester).
In first differentiation we take $x_A = 1 - x_B$.

In last transformation we use $x_A + x_B = 1$. 

**Partial molar volume (1)**

Differentiating the last equation: 

$$V = x_A \bar{V}_A + x_B \bar{V}_B$$

with respect to $x_B$:

We get:

$$\frac{dV}{dx_B} = -\bar{V}_A + x_A \frac{d\bar{V}_A}{dx_B} + \bar{V}_B + x_B \frac{d\bar{V}_B}{dx_B}$$

From G-D equation (for partial molar volumes) we have:

$$x_A d\bar{V}_A + x_B d\bar{V}_B = 0$$

what, after dividing both sides by $dx_B$ gives:

$$x_A \frac{d\bar{V}_A}{dx_B} + x_B \frac{d\bar{V}_B}{dx_B} = 0$$

and:

$$\frac{dV}{dx_B} = \bar{V}_B - \bar{V}_A$$

what permits to write first equation as:

$$V = x_A \left( \bar{V}_B - \frac{d\bar{V}}{dx_B} \right) + x_B \bar{V}_B$$

and:

$$\bar{V}_B = V + x_A \frac{dV}{dx_B}$$

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Partial molar volume (2)

An analogical procedure permits to obtain:

$$\bar{V}_A = V - x_B \frac{dV}{dx_B}$$

Both equations ( $$\bar{V}_B = V + x_B \frac{dV}{dx_B}$$ ) permit to determine $$\bar{V}_B$$ i $$\bar{V}_A$$

On the basis of experimentally measured values of solution $$V$$.

One can do it either graphically or numerically, finding for each $$x_B$$ a derivative from the plot of $$V(x_B)$$ and calculate both partial molar quantities from the above given formulæ.

$V$ to oczywiście pochodne $dV/dx_B$. 

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Contraction. What volume of vodka one can get from ½ l of water and ½ l of ethanol?

The reasons of such shapes of the curves are possible to explain (difficult). Such studies permit to determine molecular interactions in solutions.
Partial molar enthalpy (1)

One can not determine absolute enthalpy of solution, but it is possible to find enthalpy of mixing (forming of solution from pure components):

\[ \Delta h = h - (n_A H_A + n_B H_B) \]

Corresponding partial derivatives are equal to:

\[ \left[ \frac{\partial (\Delta h)}{\partial n_A} \right]_{n_B} = H_A - H_A^0 \]

Because:

\[ \left[ \frac{\partial h}{\partial n_A} \right]_{n_B} = H_A \]

Hence, differential heats of dissolution:

\[ Q_A = \left[ \frac{\partial (\Delta h)}{\partial n_A} \right]_{n_B} = H_A - H_A^0 \]

\[ Q_B = \left[ \frac{\partial (\Delta h)}{\partial n_B} \right]_{n_A} = H_B - H_B^0 \]

Enthalpy, \( \Delta h \), in the first paragraph, is known as the total (integral) heat of mixing. \( h \) is enthalpy of solution, \( H_A \) and \( H_B \) are molar enthalpies of pure components. Apparently, partial molar enthalpies are also differentials at \( P, T = \text{const} \).

Differential heat of dissolution corresponds to heat evolved or consumed when 1 mole of a component is added to infinitely large volume of solution of given concentration.

Dla składnika uważanego za rozpuszczalnik różniczkowe ciepło rozpuszczania nazywamy ciepłem rozcieńczania.

Różniczkowe ciepło rozpuszczania dla roztworu nieskończenie rozcieńczonego nazywamy „pierwszym ciepłem rozpuszczania”, a dla roztworu nasyconego – „ostatnim ciepłem rozpuszczania”.

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**Partial molar enthalpy (2)**

Because: $h = n_A H_A + n_B H_B$  
then: $\Delta h = n_A \left( H_A - H_A^0 \right) + n_B \left( H_B - H_B^0 \right)$

What, after dividing both sides by $n_A + n_B$ and substituting differential heats of dissolution, gives:

$$\Delta H = x_A \overline{Q}_A + x_B \overline{Q}_B$$

where $\Delta H$ is molar heat of mixing (dissolution).

One can determine them using calorimetric methods and analyze the data in the same way as we had done it with partial molar volumes, that does not permit us, however, to find partial molar enthalpies of components in solution, but the differential heats of dissolution only.

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Molar heat of mixing is heat gained or lost when 1 mole of solution is obtained.
Chemical potential

For solution at equilibrium with its saturated vapour:

in vapour: \[ \mu_{A,g} = \mu_{A,g}^0 + RT \ln \frac{f_A}{P^0} \]

in solution: \[ \mu_A = \mu_{A,g}^0 + RT \ln \frac{f_A}{P^0} \]

over pure component A \[ \mu_{A,g}^* = \mu_{A,g}^0 + RT \ln \frac{f_A^0}{P^0} \]

in pure liquid A: \[ \mu_A^0 = \mu_{A,g}^0 + RT \ln \frac{f_A^0}{P^0} \]

Finally, after subtracting both sides of the right equations:

\[ \mu_A - \mu_A^0 = RT \ln \frac{f_A}{f_A^0} \approx RT \ln \frac{P_A}{P^0} \]

\[ \mu_B - \mu_B^0 = RT \ln \frac{f_B}{f_B^0} \approx RT \ln \frac{P_B}{P^0} \]

Absolute value of this function (partial molar Gibbs free energy) for a component of solution is, again, unobtainable, but it is possible to find the difference between its value in solution at given concentration and its value at certain arbitrary standard state.


Zastąpienie lotności prężnościami jest całkiem uzasadnione.

\( \mu_A^0 \) to molowa entalpia swobodna czystego składnika.
A possibility exists to find absolute values of partial molar entropies of solution components (III law of thermodynamics).
Perfect (ideal) solutions

Perfect solution is a solution for which Raoult’s law is obeyed by both components over full range of compositions.

\[ P_A = P_A^0 x_A \quad \quad P_B = P_B^0 x_B \]

One can prove thermodynamically that if one component of solution obeys Raoult’s law, then the second component also must obey it.
Chemical potential of perfect solutions

If in equations:
\[
\mu_A - \mu_A^0 = RT \ln \frac{P_A}{P_A^0} , \quad \mu_B - \mu_B^0 = RT \ln \frac{P_B}{P_B^0}
\]
we use Raoult’s law, then we obtain:
\[
\mu_A = \mu_A^0 + RT \ln x_A , \quad \mu_B = \mu_B^0 + RT \ln x_B
\]

It permits us to calculate the \( \Delta g \) of mixing:
\[
\Delta g = n_A \mu_A + n_B \mu_B - n_A \mu_A^0 - n_B \mu_B^0
\]
\[
\Delta G = x_A (\mu_A - \mu_A^0) + x_B (\mu_B - \mu_B^0)
\]
\[
\Delta G = RT (x_A \ln x_A + x_B \ln x_B)
\]

\( \mu_A^0 \) i \( \mu_B^0 \) are molar free Gibbs enthalpies of pure components.

Please, notice the analogy of the equation obtained with the equation for free Gibbs energy of mixing of perfect gases.
Thermodynamic functions of mixing (1)

If we differentiate both sides of the equation: \[ \mu_A = \mu_A^0 + RT \ln x_A \]
With respect to \( T \) at constant \( P \), we get:

\[ \left( \frac{\partial \mu_A}{\partial T} \right)_P = \left( \frac{\partial \mu_A^0}{\partial T} \right)_P + R \ln x_A \]

because:

\[ \left( \frac{\partial \mu_A}{\partial T} \right)_P = -S_A \left( \frac{\partial \mu_A^0}{\partial T} \right)_P = -S_A^0 \]

then (for both components):

\[ S_A = S_A^0 - R \ln x_A \quad S_B = S_B^0 - R \ln x_B \]

and molar entropy of mixing:

\[ \Delta S = x_A (S_A - S_A^0) + x_B (S_B - S_B^0) = -R (x_A \ln x_A + x_B \ln x_B) \]
**Thermodynamic functions of mixing (2)**

*Partial molar enthalpy*

Multiplying both sides of this by $T$: $\bar{S}_A = S_A^0 - R \ln x_A$

After transformation we get: $S_A^0 T - \bar{S}_A T = RT \ln x_A$

Combining with: $\mu_A = \mu_A^0 + RT \ln x_A$ we get: $\mu_A^0 + S_A^0 T = \mu_A + \bar{S}_A T$

That leads to conclusion: $H_A^0 = H_A$ and also: $H_B^0 = H_B \Delta H = 0$

*Partial molar volume*

Differentiating both sides with respect to $P$ at constant $T$: $\mu_A = \mu_A^0 + RT \ln x_A$ we get:

$$\left( \frac{\partial \mu_A}{\partial P} \right)_T = \left( \frac{\partial \mu_A^0}{\partial P} \right)_T$$

That means: $V_A^0 = V_A$ and also: $V_B^0 = V_B \Delta V = 0$
Thermodynamic functions of mixing (3)

Perfect solution @ 298,15 K
Reasons of positive and negative deviations from Rault’s low are consequence of molecular interactions in solution.

One can derive all the thermodynamics of perfect solutions (including Raoult’s law) using statistical statystycznej, at the following assumptions:

1. Molecular interactions AA, BB and AB are approximately equal,
2. Molar volumes of A and B are approximately equal.

If interactions AB are stronger then AA and BB, then deviations from the Raoult’s law should be negative (ad vice versa).

Positive deviations may be observed, first of all, in cases, when pure components form associates (e.g. dimers), which are destructed during mixing. This is seen on the graph, where endothermic process of hydrogen bonds breaking in methanol is visible during dilution with carbon tetrachloride. Entropy, is still rather big, yet altogether Gibbs free enthalpy is significantly lower then for the perfect solution.
Oba te związki tworzą słabe wiązania wodorowe (niewielkie odchylenia ujemne), obniżenie entropii mieszania (znaczące), entalpia swobodna zmienia się niewiele, bowiem jest jednak wyraźny efekt cieplny (kompensujący małą zmianę entropii). Jest to klasyczne współdziałanie efektu entalpowego i entropowego.
Concept of regular solution, when $H^E \neq 0$ but $S^E = 0$.

For example, one can see contraction beatifully on a $V^E$ plot.
Real solutions (3)

Disregarding the reasons of deviations from the Raoult’s law one can observe, that:

1. For \( x_i \to 1 \) \( P_i \to P_i^0 \cdot x_i \) (Raoult’s law)
2. For \( x_i \to 0 \) \( P_i \to k_i \cdot x_i \) (Henry’s law)

A solution, whose components obey both the regularities is known as a perfectly diluted solution.

The solvent – obeys Raoult’s law

The solute – obeys Henry’s law

This may be proven thermodynamically.
Chemical potentials in real solutions

We know already for the solvent: \( \mu_A = \mu_A^0 + RT \ln x_A \)

For the solute we can again consider it is at equilibrium with its vapour, when:

\[
\begin{align*}
\mu_B &= \mu_{B,g}^0 + RT \ln \frac{P_B}{P^0} \\
\mu_B &= \mu_{B,g}^0 + RT \ln \frac{k}{P^0} + RT \ln x_B \\
\mu_B &= \mu_B^\circ + RT \ln x_B
\end{align*}
\]

and introducing Henry’s law:

where: \( \mu_B^\circ \) is known as the standard chemical potential

This is a hypothetical quantity, as it would correspond to chemical potential of component B at \( x_B = 1 \), if the equation (and Henry’s law) held up this value of \( x_B \).

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Standard chemical potentials

Allowing for known relations: \( x_B = \frac{M_A}{1000} m_B \) and: \( x_B = \frac{M_A}{1000 \rho_A} c_B \)

One can write: \( \mu_B = m \mu_B^\circ + RT \ln m_B \) \( \mu_B = c \mu_B^\circ + RT \ln c_B \)

where: \( m \mu_B^\circ = \mu_B^\circ + RT \ln \frac{M_A}{1000} \) \( c \mu_B^\circ = \mu_B^\circ + RT \ln \frac{M_A}{1000 \rho_A} \)

Standard chemical potentials in molality and molar concentration scales are also hypothetical quantities, as it would correspond to chemical potential of component B at \( m_B=1 \) or \( c_B=1 \), if the equations (and Henry’s law) held up these values.

These relations were developed in lecture on colligative properties in previous semester.
Real solutions at high concentrations are neither perfect solutions nor perfectly diluted ones. How to describe the thermodynamics of such systems? One opportunity are excess functions. Activities (Lewis) are another possibility – used most frequently.

**Thermodynamic definition of activity (1)**

If both components of the solution are liquids, then their activities are defined accordingly:

\[
\begin{align*}
\mu_A &= \mu_A^0 + RT \ln a_A \\
\mu_B &= \mu_B^0 + RT \ln a_B \\
a_A &= e^{\frac{\mu_A - \mu_A^0}{RT}} \\
a_B &= e^{\frac{\mu_B - \mu_B^0}{RT}}
\end{align*}
\]

Measure of activity is measurable difference between chemical potential of a component in solution and in standard state (in this case – pure compound).

In case of perfect solutions activities are equal to molar fractions.

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**Activity coefficients (1)**

Współczynniki aktywności definiuje się:

\[
\gamma_A = \frac{a_A}{x_A} \quad \gamma_B = \frac{a_B}{x_B}
\]

\[
\mu_A - (\mu_A^0 + RT \ln x_A) = RT \ln \gamma_A \quad \mu_B - (\mu_B^0 + RT \ln x_B) = RT \ln \gamma_B
\]

To różnica potencjału chemicznego składnika w roztworze rzeczywistym i tego jaki by składnik ten miał, gdyby roztwór był roztworem doskonałym.
As you see, there are different scales of activity for the solutes (rational scale for $x$).

Differences between the chemical potential of a compound in solution and in standard state are still measurable.
Activity coefficients (2)

Activity coefficients (in due scale) of a solute are defined as:

\[ x_\gamma_B = \frac{x a_B}{x_B} \quad m_\gamma_B = \frac{m a_B}{m_B} \quad c_\gamma_B = \frac{c a_B}{c_B} \]

\[ \mu_B - (x_\mu_B^\circ + RT \ln x_B) = RT \ln x_\gamma_B \] (it may be also written for the other scales)

\[ RT \ln x_\gamma_B \]

(in every scale) it is the difference between the chemical potential of the solute in a real solution and its value if the solution was a perfectly diluted one.
Thermodynamic definition of activity (3)

For solvent:

\[ a_A \to x_A \]
\[ \gamma_A \to 1 \]
when
\[ x_A \to 1 \]

For solute:

\[ a_B \to x_B(m_B, c_B) \]
\[ \gamma_B \to 1 \]
when
\[ x_B(m_B, c_B) \to 0 \]
Determination of activity

(1)

Comparing equations:

\[ \mu_A - \mu_A^0 = RT \ln \frac{f_A}{f_A^0} \approx RT \ln \frac{P_A}{P_A^0} \]

\[ \mu_A - \mu_A^0 = RT \ln a_A \]

Permit to write:

\[ a_A = \frac{f_A}{f_A^0} = \frac{P_A}{P_A^0} \]

This permits to determine activity on the basis of measuring partial pressures in a saturated vapour over the solution.

And – combined with the G-D equation:

\[ n_A d \ln a_A + n_B d \ln a_B = 0 \]

- permits to determine – using the discussed graphical method – also the activity of the second component.

Measurements are easier when the solute is non volatile.
Cryometry is used more frequently as $\Delta T$ values are larger (measurable with better accuracy).

Determination of activity (2)

Also ebuliometric and cryometric measurements permit to measure activity, as it can be proven that:

$$\ln a_a = \ln \frac{P_a}{P_a^0} = -\frac{\Delta H_b}{R T^2} \Delta T$$

$$\ln a_a = -\frac{\Delta H_m}{R T^2} \Delta T$$

Subsequently, using the G-D equation permits to determine activity of the other component.
**Dependence of activity coefficients on temperature**

One can prove that – if activities are standardized in the same way:

\[
\left( \frac{\partial \ln \gamma_A}{\partial T} \right)_p = -\frac{H_A - H_A^0}{RT^2} \quad \left( \frac{\partial \ln \gamma_B}{\partial T} \right)_p = -\frac{H_B - H_B^0}{RT^2}
\]

where the numerator of the fraction at the right side, known as the relative partial molar enthalpy of dissolution is equal to the differential heat of dissolution. However, if substance B is standardized vs, perfectly diluted solution (as a solute), then:

\[
\left( \frac{\partial \ln \gamma_B}{\partial T} \right)_p = -\frac{H_B - H_B^0}{RT^2} \quad \text{Where the numerator of the fraction is equal to the first heat of dissolution of B.}
\]
Howgh!!!