Teaching Thermodynamics - A New Concept

Regina Rüffler, Georg Job

**Job-Foundation (www.job-foundation.org), University of Hamburg,
Institute of Physical Chemistry, Grindelallee 117, 20146 Hamburg, Germany**
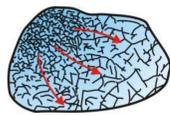
WANTED
Entropy S



- visualized as an in matter distributed,
- more or less mobile,
- *producible* but *indestructible* entity.

These assumptions allow us to describe entropy as a substance-like characteristic which can be taught in an analogous manner as the electrical charge.

1) Each object contains more or less entropy. Identical objects in the same state contain identical amounts of entropy.
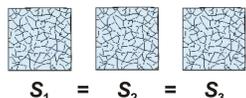
"Entropy is a state variable."

$$S_1 = S_2 = S_3$$

2) The entropy contained in an object that is composed of pieces, is the sum of the entropies of its parts.
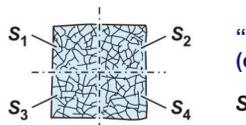
S_1 S_2

S_3 S_4

"Entropy is a substance-like (extensive) variable."

$$S_{total} = S_1 + S_2 + S_3 + S_4$$

**3)** Entropy can be produced by nearly all kinds of real processes but not destroyed.

friction   forging   irradiation

4) Entropy can<u>not</u> penetrate thermally insulating walls.

insulation

Therefore, the amount of entropy in an isolated system cannot decrease but only increase.

$$\Delta S \geq 0$$

also known as "2nd law of thermodynamics"

5) The main effect of increasing entropy is that the matter becomes *warmer*. In a set of identical objects the one without entropy is absolutely cold.
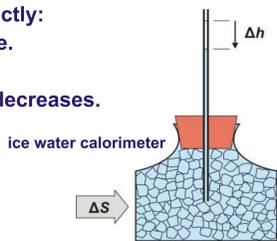
hot   warm   cold   absolutely cold

$S = 0$
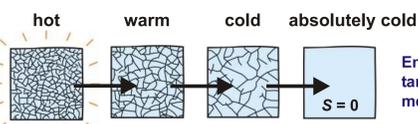
Entropy flows spontaneously from a warmer to a colder object.

Measuring entropy:

Entropy can be measured directly:
- Entropy flows into the bottle.
- A little bit of ice melts.
- The volume of the mixture decreases.
- The water level falls.

Δh

ice water calorimeter

$\Delta h \sim$ amount of entropy

ΔS

unit: 1 Ct (Carnot) = 1 J/K

Teaching

Georg Job, Regina Rüffler
Physikalische Chemie
Eine Einführung nach neuem Konzept mit zahlreichen Experimenten

As one project of the Eduard-Job-Foundation of Thermo- and Matter-dynamics a textbook "Physical Chemistry" for undergraduates is currently written
- that includes more than hundred simple but nevertheless impressive demonstration experiments and
- considers particularly the new concept.

Additionally, all experiments will be tested carefully and detailed instructions (including safety aspects and disposal procedures) as well as videos will be prepared.

The new concept induced other autors to rephrase thermodynamics or even the whole concept of physics. These conceptional changes have a strong impact not only on the education of chemists, physists, and engineers

THE DYNAMICS OF HEAT

but also on physics and chemistry classes at every level of education.

Thermodynamics is generally considered a difficult science - not only by students. Due to its historical development this discipline has a complicated and abstract structure which is generally incompatible with those of other areas of chemistry and physics thereby making an intuitive understanding difficult.

It seems that two thermodynamic quantities are especially difficult to grasp: the entropy S and the chemical potential μ. But in fact, both quantities are compatible with a layperson´s perception. Therefore, as a fast and easy way, without frightening mathematics, both quantities are introduced by a phenomenological description complemented by a direct measuring procedure, in the same way as the basic quantities length, time or mass.

REWARD ($5,000.00) "BILLY THE KID" DEAD OR ALIVE "BILLY THE KID"

For characterising an object or a person a few informations are often sufficient. The wanted poster of a person represents an example of a concise list of such "phenomenological" characteristics.

new didactic concept

Entropy S as heat μ Chemical Potential μ
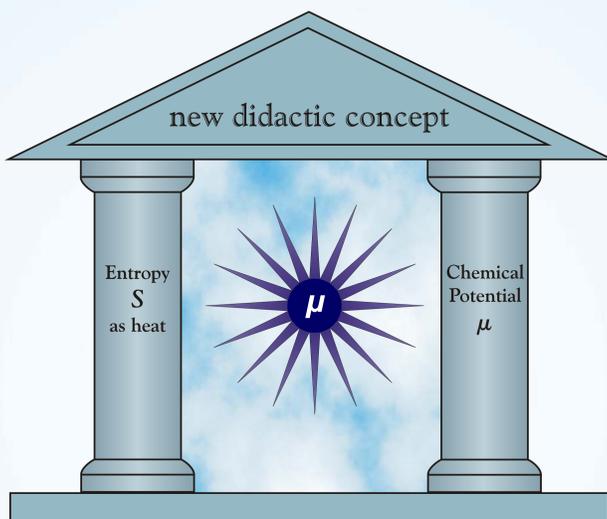
Unified Description

All calculations base on a single equation, the "*main equation*" of the system.

Example: Falling rain drop

$$dW = -pdV + TdS + \mu dn + \varphi dq + \sigma dA + vdp + md\psi \dots$$

The intensive quantity related to a *substance-like quantity* may be regarded as a *potential* acting on this quantity:

m	mass	ψ	gravitational potential
q	charge	φ	electric potential
n	amount of subst.	μ	chemical potential
p	momentum	v	"kinetic potential"
S	entropy	T	"thermal potential"

The transport of a substance-like quantity from a low potential (1) to a high potential (2) consumes energy:

m	$W = m(\psi_2 - \psi_1)$,	q	$W = q(\varphi_2 - \varphi_1)$,
n	$W = n(\mu_2 - \mu_1)$,	p	$W = p(v_2 - v_1)$,
S	$W = S(T_2 - T_1)$.		

high (2)

low (1)

The reverse process (from high (1) to low potential (2)) releases energy ($W < 0$ from the point of view of the system). Only a fraction η of this energy can be used while the rest is "burnt up" on entropy production:

$$W = \eta W + (1-\eta)W \qquad (0 \leq \eta \leq 1)$$

used energy   "burnt up" energy

produced entropy: $S_c = -(1-\eta)W/T$

An efficiency of 100% ($\eta = 1$) can be obtained only theoretically. Only these processes are *reversible*.

The production of S_c always results in an additional *warming* of the system and/or its surrounding compared to the reversible process.

For using the released energy special apparatus, machines or devices have to be applied, for example:
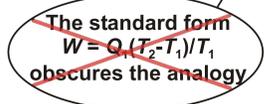
Water mill
$W = m(\psi_2 - \psi_1)$

Steam engine
$W = S(T_2 - T_1)$

"Drinking duck"
$W = n(\mu_2 - \mu_1)$

The standard form
$W = Q(T_2 - T_1)/T_1$
obscures the analogy

WANTED
Chemical Potential μ

1) The tendency of a substance A
- to *react* with other substances,
- to *transform* into another state,
- to *redistribute* in space,

can be expressed by the same quantity - namely μ_A.

2) The magnitude of this tendency, meaning the numerical value of μ_A
- is determined by the *nature* of the substance
- and by its *milieu* (temperature, pressure, concentration, solvent, field strength, ...),
- but <u>not</u> by the nature of the reaction partners or the resulting products.

3) A *reaction, transformation, redistribution* proceeds only spontaneously if the tendency for the process is more pronounced in the initial state than in the final state.

Just the sum of the "weights" G on each side – positive or negative ones – determines, to which side the seesaw leans.

negative weight

A'' A''' A' B' B'' B''' B''''

$3O_2$ $2CO_2$ $2(CH)_x$ $2H_2O$

The sum of the chemical potentials μ on each side of the reaction formula

$$A' + A'' + \dots \qquad B' + B'' + \dots$$

– positive or negative ones – determines, in which direction a reaction tends.

A reaction can run spontaneously if the potential difference between the initial and the final state is positive, i.e. if a potential drop exists.
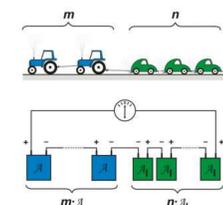
introduction of the quantity *"chemical drive"* $\mathcal{A}$
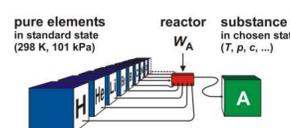
$$\mathcal{A} = \mu_{initial} - \mu_{final}$$

Measuring chemical potentials or drives:

The quantity $\mathcal{A}$ can be measured directly by coupling to a "unit reaction" $\mathcal{A}_l$ with known drive, e.g. electrically (comparable to oppositely coupled vehicles)

m n

$m \cdot \mathcal{A}$ $n \cdot \mathcal{A}_l$

$$\mathcal{A}_{total} = m \cdot \mathcal{A} + n \cdot \mathcal{A}_l = 0 \qquad \text{or}$$

$$\mathcal{A} = -(n/m) \cdot \mathcal{A}_l$$

Theoretical setup for indirect metrization of μ:

pure elements in standard state (298 K, 101 kPa)   reactor W_A substance A in chosen state ($T, p, c, \dots$)

H   A

measure of μ_A: energy W_A necessary for formation of 1 mol of substance A

$$\mu_A = W_A/n_A$$

unit: 1 G (Gibbs) = 1 J/mol

The chemical potential has a **key position** in dealing with chemical problems and starting from this central quantity it is possible to explore many other fields up to quantum statistics. As one of many examples we will discuss the

Mass Action

A linear approach can be chosen if the concentration change Δc is small:

$$\mu = \mu_0 + \gamma \cdot \Delta c$$

The more concentrated the action the more intense the effect. This is also valid for the mass action.
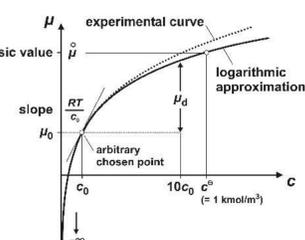
The *concentration coefficient γ* is a universal quantity, i.e. it is the same for all substances in every milieu:

$$\gamma = \frac{RT}{c} \qquad \text{(for small } c \text{ at constant } T\text{)}$$
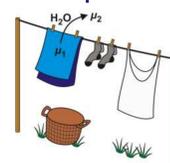
The combination of these two relations results in the so-called "*mass action equation*":

$$\mu = \mu_0 + RT\ln(c/c_0) = \mu_0 + RT\ln c_r \qquad \textit{mass action equation}$$

If the concentration c decreases one *decade* (a factor of ten), the chemical potential always decreases by the same amount, the "*deca potential*" μ_d (5.71 kG 6 kG at 298 K)

basic value

experimental curve

logarithmic approximation

slope

arbitrary chosen point

c_0 $10c_0$ c° (= 1 kmol/m³)

The concentration dependence of μ explains for example the evaporation of water at room temperature.

$H_2O|l$ $H_2O|g$

$\mu^\ominus$ (at 298 K, 101 kPa)/kG $-237 < -229$

The strong dilution of the water vapour in air lowers the value of its chemical potential below that of liquid water.

Another and very important application is the derivation of the "*mass action law*".