Energetic and Entropic Changes in Volume Work and Chemical Reactions

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Abstract

In the present study, energetic and entropic changes are investigated on a comparative basis, as they occur in the volume changes of an ideal gas in the Carnot cycle and in the course of the chemical reaction in a lead-acid battery. Differences between reversible and irreversible processes have been worked out, in particular between reversibly exchanged entropy ($\Delta_e S$) and irreversibly produced entropy ($\Delta_i S$). In the partially irreversible case, $\Delta_e S$ and $\Delta_i S$ add up to the sum ΔS for the volume changes of a gas, and only this function has an exact differential. In a chemical reaction, however, $\Delta_e S$ is independent on reversibility. It arises from the different intramolecular energy contents between products and reactants. Entropy production in a partially irreversible Carnot cycle is brought about through work-free expansions, whereas in the irreversible battery reaction entropy is produced via activated complexes, whereby a certain, variable fraction of the available chemical energy becomes transformed into electrical energy and the remaining fraction dissipated into heat. The irreversible reaction process via activated complexes has been explained phenomenologically. For a sufficiently high power output of coupled reactions, it is essential that the input energy is not completely reversibly transformed, but rather partially dissipated, because this can increase the process velocity and consequently its power output. A reduction of the counter potential is necessary for this purpose. This is not only important for man-made machines, but also for the viability of cells.

Keywords

Exchanged Entropy, Entropy Production, Coupled Reactions, Activated Complexes, Power Output

1. Introduction

In this paper, the energy and entropy changes for two different energy transfor-

mations and the resulting work are analyzed. These are associated first with the volume changes of an ideal gas and second with the chemical reaction in a lead acid battery. The work coupled to volume changes of the gas comes up as mechanical work, while the lead-acid reaction of the battery is coupled to electrical work. The respective coupling makes it possible that the processes can in principle also be gone through reversibly.

R. Clausius recognized [1] [2] that such energy transformations are accompanied by additional changes both in the system and surroundings, which are closely related to the energetic changes and allow a statement about how much of the available energy can be transformed. He designated this new quantity entropy, also to underline its close relationship with energy. He also recognized that this quantity depends on whether a process such as the expansion work of a gas is reversible or irreversible gone through. He designated the entropy component associated with irreversibility as a non-compensated transformation [2]. It is that amount of entropy which is not determined by reversible entropy exchange between the system and surroundings but is produced by the irreversibility of the process. This result later led to the inequality $dS \geq \delta q/T$, with the equal sign referring to reversible processes only. The greater-than sign comes into play when the process being analyzed is irreversible or contains irreversible parts. Under such conditions, volume changes take place without coupling to mechanical energy, so that under these circumstances heat energy cannot be consumed for this purpose either. In chemical reactions, which proceed without coupling to any other form of energy, the available chemical energy is released as heat.

The work of L. Boltzmann, J. C. Maxwell and J. W. Gibbs gave rise to classical statistical mechanics. Here especially the Maxwell-Boltzmann distribution law is used to analyze entropy changes under reversible as well as irreversible conditions. According to Ludwig Boltzmann, the fact that molecular particles (constant number and energy) apparently strive to spontaneously occupy a larger volume is based on the fact that this drastically increases the number of possible energy distributions and thus also the probability that one of these will be realized. The distribution with maximal probability (multiplicity) is targeted spontaneously. In this case, as is known, this leads to the fact that the entire available volume is occupied by the particles. Thus, it is the enormous increase in probability that drives the free expansion of an ideal gas without any impact of force. Conversely, it would be extremely unlikely that particles would spontaneously concentrate themselves at a smaller volume.

The Maxwell-Boltzmann energy distribution does not only come into play for volume changes, but is also of special importance for the energy distribution over the particles of a given particle species. Here the partition function is of central meaning. It is given by a sum of exponential functions, the Boltzmann factors, which indicate separate energy levels. Different partition functions are mainly generated by different translational, rotational, and vibrational energies

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of non-identical molecules, for example. The possible energies are not arranged continuously, but are quantized. The total energy of all particles of a species is now distributed among these discrete energy levels in a very specific way. Namely, the relative frequencies with which particles can contain a given amount of energy decrease exponentially with increasing energy. Since the resulting exponential energy distribution has been obtained by maximizing the distribution probability, its utmost important parameter, temperature, can also be interpreted as a statistical quantity [3]. When such an energy distribution of maximal probability is achieved for all particles and particle species of a system, the system is at statistical or thermal equilibrium with temperature T.

But one of the most significant achievements of the Maxwell-Boltzmann distribution law is that it provides a relationship between the Clausius definition of entropy and the maximal distribution probability at thermal equilibrium.

The aim of this work is to elaborate in particular the differences of entropy changes between volume work and chemical reactions. For this purpose, both reversible and irreversible processes are analyzed. It will further be shown how the power output of a coupled reaction is related to its entropy production.

2. Results and Discussion

2.1. Carnot Cycle Work

In the following, the ideal gas is chosen as the working substance, because with it the mathematical description of the physical processes involved is particularly simple and comprehensible. The behavior of a monatomic ideal gas is described by the ideal gas equation, given by

$$PV = n\,\mathrm{R}\,T \tag{1a}$$

(pressure P in Pa, volume V in m³, amount of gas particles n in mol, temperature T in K; gas constant R = 8.31447 J/(mol·K)).

An energy conversion from heat energy to mechanical energy, as in this case, is always brought about by a coupled process, which consists here of a gas-filled cylinder closed off by a movable piston. Volume expansion allows volume work to be done by the gas on the surroundings, whereas volume compression requires volume work to be done by the surroundings on the gas. The piston pressure may be varied by weight forces.

During expansion, the piston pressure is reduced. Kinetic energy from the gas particles is transferred to the moving piston, so that volume work can be delivered to the surroundings until the gas pressure and the changed piston pressure are in equilibrium again. The reverse process occurs during compression. Now the piston pressure is increased and the gas is compressed. In this case, volume work is performed on the gas. In the course of a work cycle, the gas absorbs heat energy from surroundings, but this can only be in part transformed into mechanical work.

For the volume work by expansion as well as compression, it is now of partic-

ular importance in which way these processes take place. In one extreme case, a maximum of work can be delivered during expansion, while a minimum of work must be expended during compression. Under such conditions, the respective process is reversible. If these extremes are not reached, the process also contains irreversible components.

From a molecular point of view, such behavior is only granted if the change in momentum during expansion is maximal. However, this means that the change in particle velocity is also at a maximum, which in turn is only ensured when the piston does not move. A piston moving in the direction of expansion would reduce this change in velocity and thus also reduce the work associated with it. During compression, the opposite happens. A piston moving in the direction of compression would transfer additional momentum to the gas particles and thus increase the work done on the gas.

This behavior will be demonstrated with a reversible and partially irreversible Carnot cycle. It consists of an isothermal (at high temperature) and subsequent adiabatic expansion, followed by an isothermal (at lower temperature) and adiabatic compression to complete the cycle. For this purpose, the following closed path of volume changes is used:

At the higher temperature Th = 310.15 K (K = Kelvin), one mole of the ideal gas has a volume of $V1$ = 0.015302 m^3 and a pressure of $P1$ = 1.685204 × 10^5 Pa (Pa = Pasqual, 1.0 bar = 10^5 Pa). The gas is now isothermally and reversibly expanded in the first step to $V2$ = 0.019069 m^3 and $P2$ = 1.352317 × 10^5 Pa. In the second step the gas is reversibly and adiabatically expanded to $V3$ = 0.023072 m^3 and $P3$ = 9.843558 × 10^4 Pa. Since no heat exchange is possible, the amount of energy corresponding to this volume work is extracted from the gas. This reduces the temperature of the system to Tc = 273.15 K. To return to the initial values (Th, $V1$ and $P1$), the gas must be compressed in the third step reversibly and isothermally at 273.15 K to $V4$ = 0.018514 m^3 and $P4$ = 1.226665 × 10^5 Pa, and in the last step adiabatically back to $V1$ and $P1$. During this fourth step the temperature of the system increases from 273.15 back to 310.15 K. Figure 1 shows the cyclic process as a P/V diagram.

Both isothermal and adiabatic curves apply only to reversible processes. Any deviation from reversibility would result in a changed course in the P/V diagram.

The work differential of isothermal volume work is given by

$$\delta W_{is} = -P(V)dV ,$$

(" δ " indicates a non-exact differential) and work W_{is} by

$$\int \delta W_{is} = W_{is} = -\int_{Vi}^{Vf} P(V)dV = -n\,R\,T\ln\left(\frac{Vf}{Vi}\right) \tag{1b}$$

(Vi = initial, and Vf = final volume).

Under adiabatic conditions, the work differential can be equated to the heat energy extracted from the gas, yielding
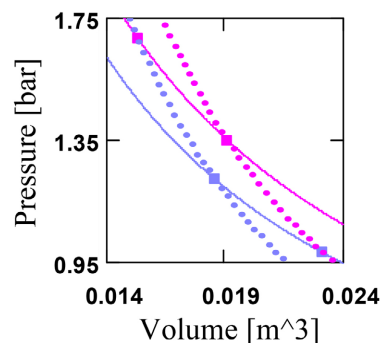
Figure 1. Reversible Carnot cycle of an ideal gas. In forward mode, the cycle begins with an isothermal expansion (Th = 310.15 K, red line) from point $P1$ to $P2$. From there, the ideal gas expands adiabatically with cooling (to Tc = 273.15 K, red points) to $P3$. At $P3$ onward, it is isothermally (at 273.15 K, blue line) compressed to $P4$, and from $P4$ onward, it is adiabatically compressed under heating (to Th = 310.15 K, blue points) back to $P1$. The enclosed area corresponds to the work reversibly done by the system.

$$-P(V)\,dV = n\,Cm_V\,dT$$

or (Cm_V = molar heat capacity at const. volume = 3/2 R (monatomic)),

$$-R\frac{dV}{V} = Cm_V\frac{dT}{T}\,.$$

Integration yields

$$-\frac{R}{Cm_V}\int_{Vi}^{Vf}\frac{dV}{V} = \int_{Ti}^{Tf}\frac{dT}{T}\,.$$

With $R = Cm_P - Cm_V$, and $\gamma = \dfrac{Cm_P}{Cm_V}$ = 1.66667 (Cm_P = molar heat capacity at const. pressure = 5/2R (monatomic),

$$Pi\,Vi^{\gamma} = Pf\,Vf^{\gamma} = PV^{\gamma} = const\,. \tag{2a}$$

is obtained.

This leads to the adiabatic work differential

$$\delta W_{ad} = -P(V)\,dV = -const.\frac{dV}{V^{\gamma}}\,,$$

and

$$\int \delta W_{ad} = W_{ad} = -const.\int_{Vi}^{Vf}\frac{dV}{V^{\gamma}}\,,$$

yielding for the adiabatic reversible work, $W_{ad} = -\dfrac{const.}{1-\gamma}\left(Vf^{(1-\gamma)} - Vi^{(1-\gamma)}\right)$, and with

$$const. = Pf\,Vf^{\gamma} = Pi\,Vi^{\gamma}\,, \tag{2b}$$

$$W_{ad} = -\frac{1}{1-\gamma}\left(Pf\,Vf - Pi\,Vi\right)\,. \tag{2c}$$

Since under adiabatic conditions the energy of expansion work cannot be re-supplied by the surroundings as heat energy as under conditions of isothermal expansion, but is extracted from the gas particles in the system, this process must be accompanied by a drop in the system's temperature from $Th = 310.15$ to $Tc = 273.15$ K. Therefore, the reversible adiabatic volume work can also be expressed through

$$W_{ad} = n\,\text{Cm}_\text{V} \int_{Ti}^{Tf} dT = n\,\text{Cm}_\text{V}\left(Tf - Ti\right). \tag{2d}$$

In the P/V diagram of **Figure 1**, the two isotherms are represented by $P_{is}(V) = n\,\text{R}\,T/V$, and the adiabats by $P_{ad}(V) = const./V^\gamma$.

2.1.1. Reversibility and Irreversibility

The derivation of the volume work with the help of infinitesimal calculus shows how the reversibility comes about and what is associated with it.

The integral of volume work is defined as follows:

$$\lim_{N\to\infty}\left(\sum_{i=1}^{N} P(V_i)\times\Delta V_i\right) = \int_{V1}^{V2} P(V)\,dV .$$

In **Figure 2** the transition from the sum of a given number of finite steps to the formation of an integral is shown by the relation given by

$$q21(N) = \frac{\sum\limits_{i=1}^{N}\left[P\left(V1 + \frac{V2 - V1}{N}\cdot i\right)\times\left(\frac{V2 - V1}{N}\right)\right]}{n\,\text{R}\,T_h \ln\left(\frac{V2}{V1}\right)} \quad (N = \text{number of steps}). \tag{3}$$

With only one expansion step (this can be achieved, for example, by expanding to $V2$ at constant final pressure $P2$), the result is a quotient of $q21(1) = 0.8976$, which means that instead of the value found by integration (-567.495 J), a reduced value of $0.8976 \times W21 = -509.391$ J is obtained. As N increases, the value of the sum approaches the value of the integral. For example, $q21(3) = 0.964$, and $q21(100) = 0.999$. The corresponding expansion works are equal to -547.111 and -556.869 J, respectively. In principle, similar results are obtained
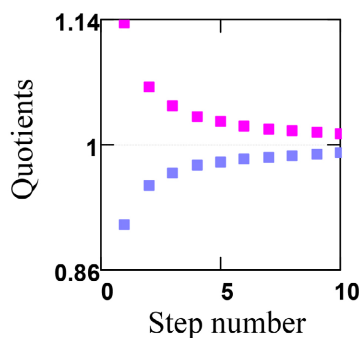

Figure 2. Work and reversibility. Blue points expansion and red points compression. Reversibility is reached when a quotient of 1.0 is reached ($N > 100$). Then the expansion work is maximal, and the compression work is minimal.

for an adiabatic expansion. The corresponding compressions, on the other hand, result in higher volume work, which now falls off when the number of steps is increased. Here, too, the value of the sum approaches the value of the integral at higher step numbers. E.g. for the reversible isothermal compression at $Tc = 273.15$ K, one obtains with a one-step compression $q43(1) = 1.1186$ and a compression work of 559.055 J, whereas a $q43(100) = 1.0011$ results in a compression work of 500.3472 J, instead of 499.7946 J by integration. In principle, the same applies to adiabatic compression.

From this behavior of the sums in comparison to their integral, it can be seen that the respective integrals always result in the maximum volume work during expansion and the minimum volume work during compression. Since only the integral over the infinitesimal changes leads to these results, it can be assumed that under real conditions reversibility can be achieved only approximately. A deviation from reversibility results in the expansion work becoming less negative and the compression work more positive. In such cases, it must be expected that the process under consideration contains both reversible and irreversible contributions.

The completely irreversible expansion of an ideal gas is of particular importance in this context. Such a situation would be realized when a gas changes, for instance at Th, from $V1$ and $P1$ to $V2$ and $P2$ by diffusion into a vacuum. In such a process, no work is done and no heat is consumed. The respective energies of all particles involved are not changed by this, so that also the temperature remains unchanged. Such a process of free expansion is considered totally irreversible. A recompression of the gas without energy input, *i.e.* a spontaneous concentration of the particles from $V2$ to $V1$, has never been observed. It can therefore be stated as an empirical theorem that a process such as the free expansion of an ideal gas is completely irreversible. However, there is no direct proof of this.

2.1.2. The Reversible Carnot Cycle

In the following, the reversible Carnot cycle will be treated first. Its thermodynamic functions such as internal energy U, enthalpy H, Helmholtz energy A, Gibbs energy G, and entropy S will be defined. Such a reversible cycle may start in the 1st step with a reversible isothermal expansion. The expansion work delivered is given by (Equation (1b)),

$$W21 = -n\,\mathrm{R}\,Th\ln\left(\frac{V2}{V1}\right) = -567.4951\,\mathrm{J}\,.$$

In order for the temperature to remain constant, the energy given off as mechanical work must be replaced by heat energy. To ensure this, the system absorbs heat from the surroundings (heat reservoir at high temperature $Th = 310.15$ K). The absorbed heat is given by,

$$Q21 = -W21 = 567.4951\,\mathrm{J}\,.$$

The 2nd step consists of an adiabatic expansion. The expansion work is given by (Equation (2c)),

$$W32 = -\frac{1}{1-\gamma}(P3V3 - P2V2) = n\,Cm_v\,(Tc - Th) = -461.4532\,\text{J}\,.$$

Since no heat can be exchanged, $Q = 0$. As already mentioned, the heat energy corresponding to the work done is extracted from the gas, so that the temperature of the system becomes decreased from $Th = 310.15$ to the colder temperature $Tc = 273.15$ K.

The next two compression steps return the system to its initial state (Th, $V1$, $P1$). This allows the process to be run repeatedly. The work input of the 3rd step via isothermal compression is given by,

$$W43 = -n\,\text{R}\,Tc\ln\left(\frac{V4}{V3}\right) = 499.7946\,\text{J}\quad\text{(according to Equation (1b))},$$

and

$$Q43 = -W43 = -499.7946\,\text{J}\,.$$

In the case of isothermal compression, the system absorbs work from surroundings. The associated energy is now released into the surroundings (reservoir of lower temperature $Tc = 273.15$ K) as heat energy to keep the temperature constant.

Then, in the 4th step, the system is adiabatically compressed so that it can assume the initial values mentioned above. This compression work is given by (Equation (2c))

$$W14 = -\frac{1}{1-\gamma}(P1V1 - P4V4) = n\,Cm_v\,(Th - Tc) = 461.4532\,\text{J}\,.$$

Obviously $W14 = -W32$. This result for a reversible cycle can be obtained from the ideal gas law, $P1V1 = P2V2$, and $P3V3 = P4V4$. It follows that $P1V1 - P4V4 = P2V2 - P3V3$, which is equal to $W14 = -W32$.

With the help of the adiabatic relations one also obtains $P2 = P3\left(\dfrac{V3}{V2}\right)^{\gamma}$, and

$P4 = P1\left(\dfrac{V1}{V4}\right)^{\gamma}$, yielding $\dfrac{V1}{V2}\dfrac{V3}{V4} = \left(\dfrac{V3}{V2}\right)^{\gamma}\left(\dfrac{V1}{V4}\right)^{\gamma}$, and

$V1^{(1-\gamma)}V2^{(\gamma-1)} = V3^{(\gamma-1)}V4^{(1-\gamma)}$. This leads to the relation

$$\frac{V2}{V1} = \frac{V3}{V4}\,. \tag{4}$$

2.1.3. Thermodynamic Functions and Volume Changes

The differential of the inner energy U of a system is known as

$$dU = \delta Q + \delta W = \delta Q - PdV\quad\text{(volume work only),} \tag{5a}$$

With $H = U + PV$ you get

$$dH = dU + d(PV), \tag{5b}$$

and for $P = \text{const.}$

$$dH = \delta Q .$$

For an ideal gas at T = const. it holds that, $d(PV) = n\,\mathrm{R}\,dT = 0$, which gives $dH = dU$ under isothermal conditions.

Under reversible conditions δQ can be replaced by $Td_e S$.

With $A = U - TS_e$, you get

$$dA = dU - d(TS_e) = -S_e dT - PdV , \tag{5c}$$

and for an ideal gas at T = const., $dA = \delta W^{rev}$.

This means that under these conditions the integral over dA represents the maximum (minimum) work ΔA.

With $G = H - TS_e$, you get

$$dG = dH - d(TS_e) = -S_e dT + VdP , \tag{5d}$$

and at T = const., $dG = \delta W^{rev}$ ($d(PV) = 0$).

That is under these latter conditions the maximum (minimum) work is given by ΔG.

Under adiabatic conditions (δQ and $d_e S$ are equal to zero),

$$dU = \delta W^{rev} , \tag{6a}$$

$$dH = dU + d(PV) = \delta W^{rev} + n\,\mathrm{R}\,dT , \tag{6b}$$

$$dA = -PdV - S_e dT , \tag{6c}$$

and

$$dG = VdP - S_e dT . \tag{6d}$$

Using the above relationships, the respective changes in all relevant thermodynamic functions can now be calculated. The change of U is given by (Equation (5a)).

For the 2nd step, since no heat is exchanged (Q = 0, Equation (6a)), you get

$$\Delta U32 = n\,Cm_V\,(Tc - Th) = W32 = -461.4532\ \mathrm{J} .$$

For the 3rd step (Equation (5a)),

$$\Delta U43 = Q43 + W43 = -499.7946 + 499.7946 = 0\ \mathrm{J} ,$$

and for the 4th step (Equation (6a)),

$$\Delta U14 = nCm_V\,(Th - Tc) = 461.4532\ \mathrm{J} .$$

When all integrals are summed over the four steps of the cycle, the line integral over a closed path is obtained. For the changes of U it is given by

$$\sum_{i=1}^{4} \Delta U_i = \oint dU = \Delta U21 + \Delta U32 + \Delta U43 + \Delta U14 = 0\ \mathrm{J} .$$

From the fact that the line integral over dU of the whole cycle (closed path) vanishes, according to the rules of differential calculus shows that it is an exact differential. This apparently does not apply to δQ and δW,

$$\sum_{i=1}^{4} Q_i = \oint \delta Q = Q21 + Q32 + Q43 + Q14 ,$$
$$= 567.4951 + 0 + (-499.7946) + 0 = 67.7 \text{ J}$$

and

$$\sum_{i=1}^{4} W_i = \oint \delta W = W21 + W32 + W43 + W14 .$$
$$= -567.4951 - 461.4532 + 499.7946 + 461.4532 = -67.7 \text{ J}$$

Since the line integrals over δQ and δW, respectively, do not vanish, these differentials are considered as non-exact.

The reversibly exchanged heat energies $Q21 = n \, R \, Th \ln(V2/V1)$ and $Q43 = n \, R \, Tc \ln(V4/V3)$ are unequal because of the different temperatures occurring in the formulas ($Th > Tc$). The quantities $n \, R \ln(V2/V1)$ and $n \, R \ln(V4/V3)$, however, are opposite equal. It has already been derived above that in the present Carnot cycle, $V2/V1 = V3/V4$. That means that these expressions $Q21/Th$ and $Q43/Tc$ resulting from the reversible heats $Q21$ and $Q43$ by division with the respective temperature can be represented as outcomes of a new function which cancel each other. The line integral hence vanishes, which means that the differential of this new function must be exact. The functional relation, recognized by R. Clausius, has been defined by him as entropy (see Introduction), its differential is given by

$$d_e S = \frac{\delta Q}{T} \tag{7a}$$

(the index "e" indicates that this infinitesimal change of S_e is associated with reversible heat exchange). Integration yields the entropy change.

$$\int d_e S = \Delta_e S = \frac{Q}{T} . \tag{7b}$$

For the present reversible Carnot cycle, the entropy change is given by

$$\Delta_e S21 = \frac{Q21}{Th} = n \, R \ln\left(\frac{V2}{V1}\right) = 1.82974 \text{ J/K} ,$$

and

$$\Delta_e S43 = \frac{Q43}{Tc} = n \, R \ln\left(\frac{V4}{V3}\right) = -1.82974 \text{ J/K} ,$$

which results in zero for the line integral.

ΔH of the first step is obtained by integrating $dH = dU + d(PV)$. This yields

$$\Delta H21 = \int_{U1}^{U2} dU + \int_{P1V1}^{P2V2} d(PV) = 0 \text{ J} \quad (T = \text{const., ideal gas}),$$

and

$$\Delta H43 = \int_{U3}^{U4} dU + \int_{P3V3}^{P4V4} d(PV) = 0 \text{ J} .$$

For the adiabatic situation, $d(PV)$ cannot be set equal to zero, since the temperature changes during both the expansion and compression process. From $\int_{P2V2}^{P3V3} d(PV) = \int_{Th}^{Tc} n\,R\,dT = n\,R\,(T_c - T_h)$ is obtained, which has to be added to ΔU under adiabatic conditions to yield ΔH. So

$$\Delta H32 = n\,Cm_V\,(Tc - Th) + n\,R\,(Tc - Th) = n\,Cm_P\,(Tc - Th) = -769.0887\,\text{J},$$

and

$$\Delta H14 = n\,Cm_P\,(Th - Tc) = 769.0887\,\text{J}.$$

The results show that also the line integral over dH vanishes in the cyclic process, and consequently also dH is an exact differential.

Integration of $dA = dG = \delta W^{rev}$ yields for the first step (Th = const.).

$$\Delta A21 = W21 = -567.4951\,\text{J},$$

and

$$\Delta G21 = W21 = -567.4951\,\text{J} \quad \text{(maximal output work)}.$$

For the third step (Tc = const.),

$$\Delta A43 = W43 = 499.7946\,\text{J},$$

and

$$\Delta G43 = W43 = 499.7946\,\text{J} \quad \text{(minimal input work) is obtained}.$$

To integrate $dA = -PdV - S_e dT$, and $dG_{ad} = V_{ad}dP - S_e dT$, respectively, for the adiabatic steps (2nd and fourth steps), their constant entropy values must be known. They are given by [4], and can be obtained from the Sackur-Tetrode equation [3] [5],

$$S_e2 = n\,R\,\ln\left(\left(\frac{2\pi m_{He}\,k_B\,Th}{h^2}\right) \times V2 \times \left(\frac{e^{\frac{5}{2}}}{N_A}\right)\right), \tag{8a}$$

and

$$S_e4 = n\,R\,\ln\left(\left(\frac{2\pi m_{He}\,k_B\,Tc}{h^2}\right) \times V4 \times \left(\frac{e^{\frac{5}{2}}}{N_A}\right)\right) \tag{8b}$$

($N_A = 6.022137 \times 10^{23}$ particles/mol, $m_{He} = 2.003 \times 10^{-3}/N_A$ kg/He atom, $k_B = R/N_A$ J/K, $h = 6.626176 \times 10^{-34}$ Js).

For the respective variables T and V, corresponding values must be inserted into the equation, e.g. for S_e2, $T = Th$, and $V = V2$. Since $\Delta_e S32$ and $\Delta_e S14$ are zero under adiabatic conditions, the temperature change in the course of the adiabatic process is compensated by the volume change, which always occurs in opposite directions. The constant values of S_e are given by

$$S_e2 = 124.4646, \quad \text{and} \quad S_e4 = 122.6349\,\text{J/K}.$$

The respective results for ΔA of steps 2 and 4, are given by

$$\Delta A32 = n\,Cm_V\left(Tc - Th\right) - n\,S_e 2\left(Tc - Th\right) = 4.1437 \times 10^3\,\text{J}\,,$$

and

$$\Delta A14 = n\,Cm_V\left(Th - Tc\right) - n\,S_e 4\left(Th - Tc\right) = -4.076 \times 10^3\,\text{J}\,.$$

In a corresponding way, the ΔG values for these steps are found.

$$\Delta G32 = n\,Cm_P\left(Tc - Th\right) - n\,S_e 2\left(Tc - Th\right) = 3.8361 \times 10^3\,\text{J}\,,$$

and

$$\Delta G14 = n\,Cm_P\left(Th - Tc\right) - n\,S_e 4\left(Th - Tc\right) = -3.7684 \times 10^3\,\text{J}\,.$$

The line integrals over dA and dG ($\sum_{i=1}^{4}\Delta A_i$ and $\sum_{i=1}^{4}\Delta G_i$, respectively) over the cycle vanish like those over $d_e S$, dU, and dH (Table 1). Therefore, these differentials are also exact. Their respective non-infinitesimal changes ΔA and ΔG are consequently independent of the path. Under isothermal conditions, the latter work functions are equal to the volume work. However, this does not apply to adiabatic conditions. This fact in addition distinguishes the volume work from the Helmholtz and Gibbs energies, since the latter vanish over the closed path of a Carnot cycle, while the volume work can be negative, zero or positive (Table 1 and Table 2).

Table 1. Change of thermodynamic functions in the four steps of a reversible Carnot cycle.

	W [J]	Q [J]	$\Delta_e S$ [J/K]	ΔU [J]	ΔH [J]	ΔA [J]	ΔG [J]
1	−567.4951	567.4951	1.82974	0	0	−567.4951	−567.4951
2	−461.4532	0	0	−461.4532	−769.0887	4.1438×10^3	3.8361×10^3
3	499.7946	−499.7946	−1.82974	0	0	499.7946	499.7946
4	461.4532	0	0	461.4532	769.0887	-4.076×10^3	-3.7684×10^3
Σ	−67.7	67.7	0	0	0	0	0

Table 2. Change of thermodynamic functions in the four steps of a partially irreversible Carnot cycle.

	W [J]	Q [J]	$\Delta_e S$ [J/K]	ΔU [J]	ΔH [J]	$\Delta_i S$ [J/K]	$\Delta_e S + \Delta_i S$ [J/K]
1	−445.2988	445.2988	1.4358	0	0	0.1404	1.5762
2	−461.4532	0	0	−461.4532	−769.0887	0.2432	0.2432
3	643.0752	−643.0752	−2.3543	0	0	0.2813	−2.073
4	461.4532	0	0	461.4532	769.0887	0.2536	0.2536
Σ	197.776	−197.776	−0.9185	0	0	0.9185	0

Whether a differential such as dG is exact can also be assessed using Maxwell's relations [4], which are mathematically based on the theorem of Schwarz. This states that the order of taking the 2nd partial derivative is of no relevance. Accordingly, the following results for the exact differential,

$$dG(T,P) = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP ,$$

$$\frac{\partial \left(\frac{\partial G}{\partial T} \right)}{\partial P} = \partial \left(\frac{\partial G}{\partial T \, \partial P} \right) \equiv \partial \left(\frac{\partial G}{\partial P \, \partial T} \right) .$$

For an ideal gas you get,

$$dG = -S_e dT + V dP ,$$

and from this the Maxwell relation,

$$-\left(\frac{\partial S_e}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P ,$$

(indices "T" and "P" mean at constant temperature and pressure, respectively). With

$$\Delta_e S = nR \ln \left(\frac{V}{V_i} \right) = -nR \ln \left(\frac{P}{P_i} \right),$$

and

$$-\frac{\partial \left(\Delta_e S \right)}{\partial P} = -\frac{\partial S_e}{\partial P} = \frac{nR}{P} ,$$

as well as

$$\frac{\partial V}{\partial T} = \frac{nR}{P} ,$$

it follows

$$-\frac{\partial S_e}{\partial P} = \frac{\partial V}{\partial T} = \frac{nR}{P} .$$

This means that the differential of the Gibbs function $G(T,P)$ of an ideal gas is an exact differential.

The Sackur-Tetrode equation can also be used for the isothermal entropy changes. For this purpose, the entropy differences at the same temperature but different volumes must be built. They are obtained by substituting the corresponding final and initial volumes. These results found with the help of quantum statistics are identical to those of classical thermodynamics.

All function values of the 4 steps in the Carnot cycle are summarized in Table 1.

In this context, it seems worth mentioning that for each infinitesimal step, the dG value for the coupled gas/piston process is zero. This is because at each moment of force development of the gas upon the piston (e. g. expansion), this is compensated by an opposing force emanating from the piston. Each step of the

coupled process therefore takes place without net work. As a result, the gas/piston system moves quasi-statically from one equilibrium state to the next. Characteristic for the existence of an equilibrium is therefore the condition $dG = 0$.

The efficiency of the volume work of an ideal gas when it expands under reversible conditions is 1.0, as it is for any other reversible energy transformation, such as the electrochemical reaction in a battery. In the case of a cyclic (Carnot) process ($\eta = \sum W_i / Q21 = (Th - Tc)/Th = 0.1193$), however, this value is considerably lower, despite reversibility. This is due to the fact that part of the expansion work has to be expended to bring the gas back to its initial volume (as well as P and T). This is inevitable because the volume can often only increase to a very limited extent. The low efficiency is therefore not due to the underlying molecular coupling process.

2.1.4. The Partially Irreversible Carnot Cycle

In the following, irreversible steps corresponding to the four reversible steps of the Carnot cycle are cyclically gone through. Irreversibility is achieved by the fact that all four volume changes take place at constant pressure. In the case of the two expansions, this is from the very beginning the lower final pressure, while in the case of the two compressions, the higher final pressure is present. The pressure and volume changes now no longer occur in infinitesimal steps, but in just one step at a time. Under these conditions, the work obtained (expansion) or put in (compression) is not maximal (less negative) for expansion and not minimal (more positive) for compression compared to reversibility. Since all works are non-zero, the individual processes are not completely irreversible.

This time the cycle starts with the partially irreversible expansion of the ideal gas from $V1y$ to $V2$ at constant pressure $P2$. In order to also run the irreversible cycle at the same temperatures Th and Tc, the adiabatic steps must be dimensioned so that their change in inner energy causes the specified temperature difference of $310.15 - 273.15 = 37.0$ K. This cannot be achieved with the volumes $V3$ and $V1$ because ΔU would be too low for adiabatic expansion and too high for adiabatic compression. The desired temperature change can be achieved, for example, by increasing $V3$ and $V1$ to $V3y$ and $V1y$, respectively. Hence, the cyclic process starts with the isothermal expansion given by

$$W21^{irrp} = -P2(V2 - V1y) = -445.3, \tag{9a}$$

and

$$Q21^{irrp} = -W21^{irrp} = 445.3 \, \text{J}.$$

So $\Delta U21^{irrp}$ and $\Delta H21^{irrp}$ are zero also under these conditions.

For the next adiabatic step of the cycle the work done must be equal to $n\,\text{Cm}_V(Tc - Th)$, to reach the lower temperature Tc. The increased volume $V3y$ is obtained by equating $W32$ with $W32^{irrp} = P3(V3y - V2)$, yielding (9b)

$$W32 = n\,\text{Cm}_V(Tc - Th) = P3(V3y - V2), \text{ yielding}$$

$$V3y = V2 - \frac{W32}{P3} = 0.023757 \text{ m}^3 .$$

$\Delta U32^{irrp}$ and $\Delta H32^{irrp}$ have the same values as under reversible conditions because $W32^{irrp} = W32$.

The isothermal compression work at Tc is given by

$$W43^{irrp} = -P4(V4 - V3y) = -643.0752 , \qquad (9c)$$

and

$$Q43^{irrp} = -W43^{irrp} = 643.0752 \text{ J} .$$

$\Delta U43^{irrp}$ and $\Delta H43^{irrp}$ are again both equal to zero.

The final step of the partially irreversible cycle is an adiabatic compression, which again results in Th. To do this, also this time $V1$ must be enlarged to $V1y$ according to

$$V1y = V4 - \frac{W14}{P4} = 0.015776 \text{ m}^3 ,$$

and

$$W14^{irrp} = -P1(V1y - V4) = 461.4532 \text{ J} . \qquad (9d)$$

In the following, the entropy changes for the reversible and irreversible parts of the individual steps are considered separately in order to identify the changes caused by irreversibility. To determine $\Delta_e S$, the reversible fractions of all partially irreversible steps of the cycle must be found. For this purpose, the partially irreversible work is set equal to the reversible work yielding for isothermal expansion

$$P2(V2 - V1y) = nR\,Th\ln\left(\frac{V1x}{V1y}\right),$$

from which

$$V1x = V1y\, e^{\frac{P2(V2-V1y)}{nR\,Th}} = 0.01875 \text{ m}^3 ,$$

is obtained.

The reversible volume work is given by

$$W21x = -nR\,Th\ln\left(\frac{V1x}{V1y}\right) = -445.3 \text{ J} .$$

It is equal to $W21^{irrp}$, and the reversible heat is $Q21x = -W21x$, and thus,

$$\Delta_e S21x = \frac{Q21x}{Th} = nR\ln\left(\frac{V1x}{V1y}\right) = 1.4358 \text{ J/K} .$$

$V2$ would then have to be attained by increasing the gas volume from $V1x$ to $V2$ without volume work. As already mentioned, such a free expansion of an ideal gas happens without temperature change. Only the pressure of the gas would decrease to $P2$. This completely irreversible process is associated with an entropy production of

$$\Delta_i S21 = n\,\mathrm{R}\ln\left(\frac{V2}{V1\mathrm{x}}\right) = 0.1404\ \mathrm{J/K}\ .$$

Since the ideal gas expands freely under these conditions, also no work can be done. In other words, the maximal work that can be gained under reversible conditions is dissipated under completely irreversible conditions. Hence, the entropy production $\Delta_i S$ is always associated with that dissipated work under completely irreversible conditions.

The sum of both forms of entropy is given by

$$\Delta S21 = \Delta_e S21x + \Delta_i S21 = n\,\mathrm{R}\ln\left(\frac{V1\mathrm{x}}{V1\mathrm{y}}\frac{V2}{V1\mathrm{x}}\right) = n\,\mathrm{R}\ln\left(\frac{V2}{V1\mathrm{y}}\right) = 1.5762\ \mathrm{J/K}\ .$$

Obviously, the sum of both entropies has the value which the entropy would take in case of a completely reversible, isothermal expansion (from $V1\mathrm{y}$ to $V2$).

In an analogous way one finds for the partially irreversible compression,

$$V3\mathrm{x} = V3\mathrm{y}\,e^{\frac{P4(V4-V3\mathrm{y})}{n\,\mathrm{R}\,Tc}} = 0.0179\ \mathrm{m}^3\ ,$$

leading to

$$\Delta_e S43x = n\,\mathrm{R}\ln\left(\frac{V3\mathrm{x}}{V3\mathrm{y}}\right) = -2.3543\ \mathrm{J/K}\ ,$$

and

$$\Delta_i S43 = n\,\mathrm{R}\ln\left(\frac{V4}{V3\mathrm{x}}\right) = 0.2813\ \mathrm{J/K}\ ,$$

whose sum is given by

$$\Delta S43 = \Delta_e S43x + \Delta_i S43 = n\,\mathrm{R}\ln\left(\frac{V4}{V3\mathrm{y}}\right) = -2.073\ \mathrm{J/K}\ .$$

To obtain the $V\mathrm{x}$ of the adiabatic processes, the partially irreversible volume work is equated to the reversible volume work of the respective adiabatic process. For the adiabatic expansion this results in

$$V2\mathrm{x} = \left(\frac{W32\mathrm{y}(1-\gamma)}{-P2V2^{\gamma}} + V2^{(1-\gamma)}\right)^{(1-\gamma)} = 0.02307\ \mathrm{m}^3\ .$$

Thus the entropy production for this step results in

$$\Delta_i S32 = n\,\mathrm{R}\ln\left(\frac{V3\mathrm{y}}{V2\mathrm{x}}\right) = 0.2432\ \mathrm{J/K}\ .$$

For the partially irreversible adiabatic compression you get

$$V4\mathrm{x} = \left(\frac{W14\mathrm{y}(1-\gamma)}{-P4V4^{\gamma}} + V4^{(1-\gamma)}\right)^{(1-\gamma)} = 0.0153\ \mathrm{m}^3\ ,$$

and

$$\Delta_i S14 = n\,\mathrm{R}\ln\left(\frac{V4\mathrm{y}}{V4\mathrm{x}}\right) = 0.2536\ \mathrm{J/K}\ .$$

It turns out that under partially irreversible conditions the sum of the exchanged entropies, $\Delta_e S21$ and $\Delta_e S43$, is not zero as in a fully reversible cycle but negative (Table 2). Thus, the sum of irreversibly produced entropies $\Delta_i S21$, $\Delta_i S32$, $\Delta_i S43$, and $\Delta_i S14$ (each one positive), must add up to zero with the former sum (Table 2). This fact can be expressed as follows:

$$\oint_{irrp} d_e S < 0, \text{ and } \oint_{irrp} d_i S > 0, \tag{10a}$$

and

$$\Delta S_{cyc}^{irrp} = \oint_{irrp} d_e S + \oint_{irrp} d_i S = 0. \tag{10b}$$

The result of the present partially irreversible cycle is accordingly

$$\begin{aligned}&\left(\Delta_e S21 + \Delta_e S43\right) + \left(\Delta_i S21 + \Delta_i S32 + \Delta_i S43 + \Delta_i S14\right)\\&= -0.91854 + 0.91854 \,\text{J/K}\end{aligned},$$

or

$$\begin{aligned}\Delta S_{cyc}^{irrp} &= R \ln\left(\frac{V2}{V21x}\frac{V21x}{V14y}\frac{V32y}{V32x}\frac{V4}{V43x}\frac{V43x}{V32y}\frac{V14y}{V14x}\right)\\&= R\ln\left(\frac{V2}{V32x}\frac{V4}{V14x}\right) = 0\end{aligned}.$$

The above expression contains the volume ratios of the reversible portions of this cycle, which correspond to the relationship of the entirely reversible cycle ($V2/V3 \times V4/V1 = 1.0$, see above).

With ΔS, the irreversible fraction of a partially irreversible process is given by $\Delta_i S / \Delta S$. From Table 2 it can be seen that this fraction is, for example, 0.1404/1.5762 = 0.089 for the first step of the Carnot cycle, 1.0 for the second and fourth steps, and −0.1357 for the third step.

For all irreversible and partially irreversible processes, $\Delta_i S > 0$, always holds. For the partially irreversible cycle considered here, this latter statement is proved by the fact that the quotient $V_f/V\text{x}$ appearing in the respective logarithms (free expansion in each step of the cycle) is always greater than one, so that $\Delta_i S = n R \ln\left(V_f / Vx\right)$, must always be positive.

Also for the partially irreversible case, the application of the Sackur-Tetrode equation gives identical results. For instance,

$$\Delta_e S21x = S21(V1x) - S21(V1y) = 124.3242 - 122.8885 = 1.4358 \,\text{J/K},$$

and

$$\Delta_i S21 = S21(V2) - S(V1x) = 124.4646 - 124.3242 = 0.1404 \,\text{J/K}.$$

All function values of the 4 steps of the partially irreversible cycle are summarized in Table 2.

In this context, the following problem may be also of interest: How do the entropies behave in a Carnot cycle whose volume work is equal to zero? Such a cycle would be realized, for example, by increasing the isothermal compression

work to such an extent that it would be opposite equal to the isothermal expansion work. The total work of the otherwise reversible cycle would then be zero. An increase from $W43$ to $-W21$ can be achieved by enlarging the volume of $V3$ accordingly. This must be done at constant Tc by irreversible free expansion of the gas into a vacuum. The new volume from which compression now starts is given by

$$V3z = V4\left(V2/V1\right)^{Th/Tc} = 0.02377 \text{ m}^3 \quad \text{(equating } W43z \text{ with } -W21\text{),}$$

and the respective, reversible compression work by,

$$W43z = -n\,\text{R}\,Tc\ln\left(\frac{V4}{V3z}\right) = 567.4951 \text{ J .}$$

The produced entropy of the additional free expansion step is given by

$$\Delta_i S43z = n\,\text{R}\ln\left(\frac{V3z}{V3}\right) = 0.2479 \text{ J/K .}$$

However, the exchanged entropy has also changed under this new condition, it must be more negative due to the increased reversible compression work of this step,

$$\Delta_e S43z = n\,\text{R}\ln\left(\frac{V4}{V3z}\right) = -2.0776 \text{ J/K .}$$

As requested, the total entropy change over the cycle vanishes,

$$\Delta_e S21 + \Delta_e S43z + \Delta_i S43z = 1.8297 - 2.0776 + 0.2479 = 0 \text{ J/K ,}$$

or

$$\begin{aligned}
\Delta_i S43z &= -\left(\Delta_e S21 + \Delta_e S43z\right) = Q21\left(\frac{1}{Tc} - \frac{1}{Th}\right) \\
&= 567.4951\left(\frac{1}{273.15} - \frac{1}{310.15}\right) = 0.2479 \text{ J/K}
\end{aligned}$$

The same result is obtained by comparing $\Delta_e S$ values of the fully reversible with the partially irreversible step 3,

$$\Delta_e S43 - \Delta_e S43z = -1.8297 - \left(-2.0776\right) = 0.2479 \text{ J/K .}$$

Analogously, with $W21 = -W43$, and $-Q43 = 499.7946$ J, $\Delta_i S21z = 0.2182$ J/K can be obtained, and $\Delta_e S21 - \Delta_e S21z = 1.8297 - 1.6115 = 0.2182$ J/K .

This result can also be understood as entropy production by irreversible heat transfer (heat quantity = $Q21$) from a reservoir with temperature Th to a reservoir with temperature Tc. When the two compartments are connected by a heat-permeable boundary to form one single system, heat energy will flow irreversibly from compartment I with Th to compartment II with Tc. Since this process is not coupled to work, and moreover takes place at unequal temperatures, it can be expected that these are irreversible entropy changes. This leads to $\Delta_i S_h^I = -Qh/Th$, and $\Delta_i S_c^{II} = Qc/Tc$. This yields for the entire system with $Qh = Qc = Q$,

$$\Delta_i S = \Delta_i S_h^I + \Delta_i S_c^{II} = Q\left(\frac{1}{Tc} - \frac{1}{Th}\right). \tag{11}$$

Since for all pathways the molecular composition of the reservoirs has not been specified, it follows that the entropy production by irreversible heat transfer is independent of the molecular structure of the media in which it takes place.

Though irreversibility and associated entropy production in energy conversions always leads to reduced efficiency, it also offers indispensable advantages. In technology, it is not the energy but the power output—*i.e.* the provision of energy per unit of time or, for mechanical processes, the speed at which a force is available—that is of primary interest. In living organisms, too, the ability to deliver power is of utmost importance. This ability is inevitably linked to entropy production ($\Delta_i S$). Therefore, in order to gain a certain amount of power from a process, it is imperative to run it partially irreversibly.

2.2. Chemical Reactions

Irreversibility is particularly important for spontaneously extending chemical and biochemical reactions. However, before the changes of $\Delta_e S$ and $\Delta_i S$ occurring in the process can be dealt with, some aspects of the energetics of chemical reactions shall first be considered.

dU can be formulated with the inclusion of non-volume work (W^{nvw}) for reversible conditions as

$$dU = -PdV + Td_e S + \delta W^{nvw} = -PdV + Td_e S + \mu\, dn, \tag{12a}$$

where δW^{nvw} may be given e.g. by $\mu\, dn$. The newly added conjugate pair $\mu\, dn$ is composed of the chemical potential μ (in J/mol, see e.g. [6] [7] [8]) and the variable particle amount n (in mol).

You get also,

$$dH = VdP + Td_e S + \mu\, dn, \tag{12b}$$

$$dA = -PdV - S_e dT + \mu\, dn, \tag{12c}$$

and

$$dG = VdP - S_e dT + \mu\, dn. \tag{12d}$$

With $n_i = v_i \xi$ (ξ = extent of reaction in mol, v_i = stoichiometric coefficient of substance *i*), and constant *P*, the respective Maxwell relation (see above) can be formulated as follows,

$$\frac{\partial(\partial G)}{\partial T\, \partial \xi} = \frac{\partial(\partial G)}{\partial T\, \partial \xi},$$

or, since

$$\frac{\partial G}{\partial T} = -S_e,\quad \frac{\partial_e S}{\partial \xi} \equiv \frac{\partial_e S}{\partial \xi},$$

which proves that $dG(T, \xi)$ is also an exact differential for chemical reactions.

In analogy to the notation $\partial G/\partial\xi = \Delta_R G$, $\partial_e S/\partial\xi = \Delta_{Re} S$ is used here.

For constant T and V, $dA = \mu\, dn$, and for constant T and P, $dG = \mu\, dn$. Since the functions A and G refer exclusively to reversible processes, $\left(\partial A/\partial T\right)_V = -S_e$ and $\left(\partial G/\partial T\right)_P = -S_e$ are applicable to the exchanged entropy only.

If several substances are present in the system, dG is made up of the individual $\mu\, dn$'s of all substances of the system, leading to

$$dG = \left(\sum_i \mu_i\, dn_i\right)_{T,P} = \sum_i \nu_i \mu_i\, d\xi$$

(The summation symbol indicates the stoichiometric summation of products and reactants), or

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \Delta_R G = \sum_i \left(\nu_i \mu_i\right). \tag{13}$$

Inserting the expression for the chemical potentials,

$$\mu = \mu^0 + \mathrm{R}\, T \ln\left(\frac{c}{c^0}\right),$$

(in J/mol, μ^0 = reference or standard potential, ideal conditions), results in,

$$\frac{dG}{d\xi} = \Delta_R G = \sum_i \nu_i \mu_i^0 + \mathrm{R}\, T \sum_i \nu_i \ln\left(c_i\right) = \Delta_R G^0 + \mathrm{R}\, T \ln\left(\Gamma\right) \tag{14}$$

The stoichiometric sum of standard potentials is given by $\Delta_R G^0 = \sum_i \nu_i \mu_i^0$, while the expression $\mathrm{R}\, T \ln\left(\Gamma\right)$ represents the concentration dependent term of the chemical potential sum. To obtain the primitive G or ΔG, the above equation must be integrated. From Equation (14) you get,

$$\int_0^\xi dG(\xi) = \Delta G(\xi) = \int_0^\xi \Delta_R G(\xi)\, d\xi = \Delta_R G^0 \times \xi + \mathrm{R}\, T \int_0^\xi \ln\left(\Gamma(\xi)\right). \tag{15}$$

In contrast to the differential quotient $dG/d\xi = \Delta_R G$, ΔG is a difference. The difference between ΔG and $\Delta_R G$ is also apparent in their respective dimensions. ΔG is given in J, whereas $\Delta_R G$ is given in J/mol. The derivative with respect to ξ represents a potential difference. It is equal to the energy change that would be achieved if the reaction were run one mole times at constant concentrations of products and reactants.

In electrochemical reactions, electrical potentials are involved in addition to chemical ones. If these are to be taken into account, the electrochemical potential $\tilde{\mu}$ must be used instead of μ alone. It is defined as $\tilde{\mu} = \mu + \mathrm{z}\mathrm{F}\varphi$. This leads for an electrochemical reaction (P, T const.) to

$$\Delta_R G = \sum_i \nu_i \left(\mu_i + \mathrm{z}_i\, \mathrm{F}\varphi_i\right) \tag{16}$$

(z = charge number, F = Faraday constant in Coulomb/mol, φ = electrical potential in Volt (V)).

In this context, it is worth mentioning that the direction of progress of a

chemical or biochemical reaction is specified by its driving force $DF = -\Delta_R G$. A positive value indicates if a reaction can proceed into the given direction.

Coupled reactions often proceed partially irreversibly in order to achieve a certain power output, as has been already mentioned. In this case, the reversible part of the coupled overall reaction becomes reversibly transformed mostly into another form of energy (output energy), whereas the rest of the input energy ($\Delta_R G_c$ or ΔG_c) is converted into heat energy.

The dissipation function Φ is closely related to this irreversibly produced heat and entropy $\Delta_{Ri} S$. When the flux $J(\xi) = d\xi/dt$ (in mol/s) is given, one obtains with,

$$\Phi(\xi) = -\Delta_R G(\xi) J(\xi) = \frac{-dG(\xi)}{dt} = T \frac{d_i S}{dt} \; (\text{J/s}), \tag{17}$$

and

$$\Delta_{Ri} S(\xi) = \frac{\Phi(\xi)}{J(\xi) T} \tag{18}$$

Integration yields,

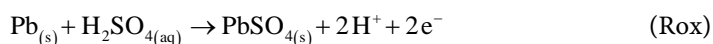$$\int_0^{\xi} \phi(\xi) dt = -\int_0^{\xi} dG(\xi) = T \int_0^{\xi} d_i S(\xi),$$

and with $dt = \dfrac{d\xi}{J(\xi)}$, and $t = \dfrac{1}{3600} \displaystyle\int_0^{\xi} \dfrac{1}{J(\xi)} d\xi$ (For comparison, the potentials are also shown against time t, see **Figure 3(a)** and **Figure 3(c)**),

$$\int_0^{\xi} \frac{\Phi(\xi)}{J(\xi)} d\xi = -\Delta G(\xi) = T \Delta_i S(\xi) \; \text{ in J.} \tag{19}$$
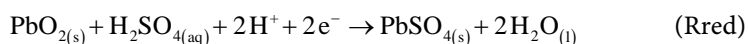
Φ indicates how much energy becomes dissipated into heat energy per unit time (Equation (17)). The time integral of this function thus gives the energy dissipated within a given time interval, which is identical to $-\Delta G = T \Delta_i S$.

2.2.1. Coupled Reactions of the Lead-Acid Battery

As an example of a coupled reaction, the electrochemical processes as they occur in a lead-acid battery are considered below. The common car battery (lead-acid battery) probably represents the most widespread man-made device in which chemical energy is transformed into electrical energy by coupling. The coupling process takes place at both electrodes. The half-reactions at the electrodes for the spontaneous discharge are given by

$$\text{Pb}_{(s)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow \text{PbSO}_{4(s)} + 2\text{H}^+ + 2\text{e}^- \tag{Rox}$$

(oxidation, anode, minus pole),

$$\text{PbO}_{2(s)} + \text{H}_2\text{SO}_{4(aq)} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_{4(s)} + 2\text{H}_2\text{O}_{(l)} \tag{Rred}$$

(reduction, cathode, plus pole), and the overall reaction by

$$\text{Pb}_{(s)} + \text{PbO}_{2(s)} + 2\text{H}_2\text{SO}_{4(aq)} \rightarrow 2\text{PbSO}_{4(s)} + 2\text{H}_2\text{O}_{(l)} \tag{Rov}$$
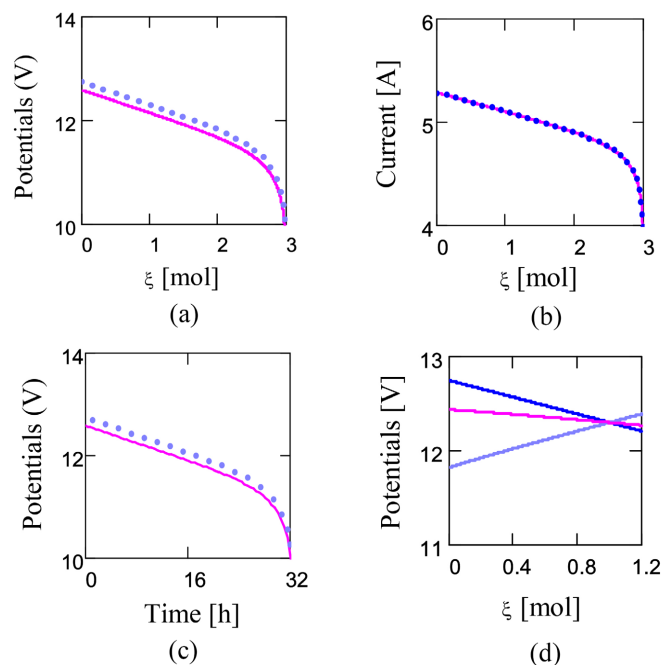
Figure 3. Potentials and electrical currents during the extending reaction (discharge) of a lead-acid battery. (a): $EMF(\xi)$ (blue points) and $-\Delta\varphi(\xi)$ (red line) in a simple circuit (G_e = 0.42 1/Ω, discharge). (b): Currents in the inner and outer current branches, respectively (inner branch: red line, outer branch: blue points). (c): as in A, but as a function of time. (d): Charging of a discharged battery by a fully charged one (see below). Red line: $-\Delta\varphi(\xi)$, dark blue line: $EMF1(\xi)$, light blue line: $EMF2(\xi)$. The potentials take the following values with ξ_{eq} = 1.0 mol: $EMF1(1.0)$ = 12.3005, $EMF2(1.0)$ = −12.3005, and $\Delta\varphi(1.0)$ = ±12.3005 V. At this ξ, equilibrium is reached between discharge and charge reactions.

The sum of both half-reactions gives the overall reaction Rov (half-reactions are usually formulated as a reduction).

The electrolyte surrounding the electrodes is an aqueous solution of sulfuric acid. In car batteries, the acid concentration is about 6.0 m (m = mol/kg H_2O, molal). When the electrodes of the battery come into contact with the electrolyte, spontaneous reactions are triggered at both electrodes (open circuit conditions). At the anode (minus pole), Pb^{2+} ions are formed from the lead atoms of the electrode by oxidation. At the cathode, Pb^{2+} ions are also formed but this time by electron uptake of the PbO_2 with the participation of H_2SO_4. In this process, the Pb^{IV} of the PbO_2 is reduced to Pb^{2+} ions. At both electrodes crystalline $PbSO_{4(s)}$ may be formed according to its solubility product. However, these electrochemical electrode reactions can only take place to a very limited extent, because electrical double layers are formed at the anode and cathode [9], whose respective electrical potential differences are opposed to the chemical potential differences of respective electrode reactions, so that both reactions very quickly reach an electrochemical equilibrium. The Gibbs potential of the overall reaction is then opposite equal to the sum of the electric potentials of the double layers.

When both poles are electrically connected via an external resistor, a current can flow that destroys the electrochemical equilibrium. Now the Gibbs potential outweighs the opposite electrical potential difference, allowing the chemical reaction and the coupled electrode reactions to proceed. The Gibbs potential of the total sulfuric acid reaction corresponding to Rov is given by,

$$\Delta_R G_{SA} = \Delta_R G_{SA}^0 + R T \ln\left(\frac{a_{H_2O}^2}{a_{H_2SO_4}^2}\right). \tag{20a}$$

The Gibbs standard reaction potential, $\Delta_R G_{SA}^0 = -394.148 \times 10^3$ J/mol, and the standard reaction enthalpy, $\Delta_R H_{SA}^0 = -315.6 \times 10^3$ J/mol, have been calculated from Gibbs formation and enthalpy formation potentials [10], respectively. The reaction entropy, $\Delta_{Re} S_{SA} = 263.35$ J/(mol·K), has been calculated from Third Law entropies [10]. The notation "a_{index}" indicates that this is not a concentration but an activity. This is essential because the electrolyte is a highly concentrated (6.0 mol/kg H_2O) aqueous solution of sulfuric acid, which deviates significantly from the properties of an ideal solution. The activity of H_2SO_4 is related to its molality m by the following definition: for a H_2SO_4 solution of molal concentration m, it is assumed that it is completely dissociated in aqueous solution into the corresponding ions according to its stoichiometric coefficients, that is $m_{H^+} = 2m$, and $m_{SO_4^{2-}} = m$. Ion activities are related to their molality through a mean activity coefficient $\gamma_\pm$,

$$a_{ion} = m_{ion}\, \gamma_\pm.$$

Single ion coefficients on the other hand are defined as

$$a_{ion} = m_{ion}\, \gamma_{ion}.$$

As a consequence, the activity of H_2SO_4 in the argument of the logarithm can be expressed as $a_{H_2SO_4} = a_{H^+}^2 a_{SO_4^{2-}} = \left(2m\gamma_\pm\right)^2\left(m\gamma_\pm\right) = 4m^3 \gamma_\pm^3$ [11], leading to

$$\Delta_R G_{SA} = \Delta_R G_{SA}^0 + R T \ln\left(\frac{a_{H_2O}^2}{\left(4m^3\gamma_\pm^3\right)^2}\right). \tag{20b}$$

With single ion activity coefficients, you would get

$$a_{H^+}^2 a_{SO_4^{2-}} = \left(2m\gamma_{H^+}\right)^2\left(m\gamma_{SO_4^{2-}}\right) = 4m^3\, \gamma_{H^+}^2\, \gamma_{SO_4^{2-}}.$$

By comparison you obtain

$$\gamma_\pm = \left(\gamma_{H^+}^2\, \gamma_{SO_4^{2-}}\right)^{\frac{1}{3}},$$

or more generally,

$$\gamma_\pm = \left(\gamma_+^{\nu_+}\, \gamma_-^{\nu_-}\right)^{\frac{1}{\nu_+ + \nu_-}}$$

(the stoichiometric coefficients of H_2SO_4 are $\nu_+ = 2$, and $\nu_- = 1$).

The mean ionic activity coefficient thus is the geometric mean of the single ionic activity coefficients.

Fraenkel [12] [13] [14] was able to calculate both mean and single ion activity coefficients using a theoretical approach. Theory and experimental results are in excellent agreement if it is assumed that H_2SO_4 and H_2O react almost quantitatively to give H_4SO_5 (sulfoxuric or parasulfuric acid, [12]). This acid exists in an aqueous solution as HSO_5^{3-} plus $3H^+$ even at high concentrations. For the following calculations, however, the chemical reactions mentioned above (Rov, Rox and Rred) are used because they are well-known and less complicated, which simplifies their treatment as a coupled reaction. Moreover, their thermodynamic data are easily accessible (e.g. in [10] [11]).

To represent $\Delta_R G_{SA}$ as a function of ξ, the activities for H_2O and H_2SO_4 must be substituted into Equation (20b). These can be found in K. R. Bullock [11] as a function of molality. Here, the values in the range between 6.0 and 1.5 m have been approximated by quadratic functions. This yields the Gibbs potential and the electromotive force, respectively, of a battery composed of six cells in series,

$$\Delta_R G(\xi) = 6\Delta_R G_{SA}^0 + 6RT\ln\left(\frac{\left(a_{H_2O}\left(\frac{n_{SA}^0 - 2\xi}{1 + 2\xi M_{H_2O} 10^{-3}}\right)\right)^2}{\left(4\left(\frac{n_{SA}^0 - 2\xi}{1 + 2\xi M_{H_2O} 10^{-3}}\right)^3\left(\gamma_\pm\left(\frac{n_{SA}^0 - 2\xi}{1 + 2\xi M_{H_2O} 10^{-3}}\right)\right)^3\right)^2}\right)$$

(20c)

and

$$EMF(\xi) = -\frac{\Delta_R G(\xi)}{zF} \text{ in Volt.}$$

(n_{SA}^0 = 6.0 mol, M_{H_2O} = 18.015 × 10⁻³ kg/mol z = 2, F = Faraday constant in coulomb/mol).

For instance, $EMF(0) = 12.7467$, and $EMF(2) = 11.8212$ V. The concentration of H_2SO_4 is $m_{SA}(\xi = 0) = \left(n_{SA}^0 - 2\xi\right)/\left(1 + 2\xi M_{H_2O} 10^{-3}\right) = 6.0$, and $m_{SA}(\xi = 2)$ = 1.865567 mol/(kg H_2O). For $\xi = \xi_{st} = 1.0092254$ mol, $\Delta_R G(\xi_{st})/6 = \Delta_R G_{SA}^0 = -3.9547 \times 10^5$ J ($\Delta_R G\Gamma_{SA}(\xi_{st})$, the logarithmic term of $\Delta_R G_{SA}(\xi_{st})$, must vanish), the standard Gibbs potential of this reaction is obtained. This means that with $n_{SA}^0 - 2\xi_{st}$ = 3.9816 mol H_2SO_4, and mass of water, $m_{H_2O}(\xi_{st}) = 1 + 2\xi_{st} M_{H_2O} 10^{-3}$ = 1.0364 kg, the H_2SO_4 concentration $m_{SA}(\xi_{st})$ = 3.8419 mol H_2SO_4/(kg H_2O), standard conditions are present.

In the following, the electric current I (in A) supplied by the battery is calculated using the flux equation known from the thermodynamics of irreversible processes [7] [15] [16] [17]. For a system consisting of two thermodynamic forces ($X1$ and $X2$) coupled to each other, the fluxes $J1$ and $J2$ are given by the flux equations

$$J1 = L11X1 + L12X2, \tag{21a}$$

and

$$J2 = L12X1 + L22X2. \tag{21b}$$

$J1$ and $J2$ are the output and input fluxes (in mol/s), respectively, $X1$ and $X2$ are the thermodynamic output and input "forces" (in J/mol). The input forces can be taken as driving forces, as they occur as affinities ($A = -\Delta_R G$) of chemical or biochemical reactions, while the output forces are often electrical or electrochemical potential differences. $L11$ and $L22$ are called straight coefficients, whereas $L12$ is called coupling coefficient.

Replacing the straight coefficients $L11$ and $L22$ by $L11 = L12 + L_{L1}$, and $L22 = L12 + L_{L2}$ (L_{L1} and L_{L2} = leak conductances, all in mol/s × mol/J), respectively, yields

$$J1 = L12(X1 + X2) + L_{L1}X1,$$

and

$$J2 = L12(X1 + X2) + L_{L2}X2.$$

With $\lambda1 = L_{L1}/L12$, and $\lambda2 = L_{L2}/L12$, you get,

$$J1 = L12(X1 + X2) + \lambda1 L12 X1,$$

or

$$J1 = L12((\lambda1 + 1)X1 + X2), \tag{21c}$$

as well as

$$J2 = L12(X1 + X2) + \lambda2 L12 X2,$$

or

$$J2 = L12(X1 + (\lambda2 + 1)X2) \quad \text{[18] [19].} \tag{21d}$$

For totally coupled systems, $\lambda1 = \lambda2 = 0$, so that $J1 = J2 = J$ results. For the totally coupled reaction flux of the lead acid battery you get,

$$J(\xi) = L_c(zF\Delta\varphi(\xi) - \Delta_R G(\xi)) \quad \text{(in mol/s),} \tag{21e}$$

($L_c \triangleq L12$ = coupling conductance, $\Delta_R G(\xi)$ = Gibbs potential and $\Delta\varphi$ = electrical potential difference (<0) of 6 cells in series) which leads with $G_c = L_c(zF)^2$ (G_c = electrical conductance (1/Ω)) to

$$I = zFJ = L_c(zF)^2(\Delta\varphi + EMF),$$

and

$$I(\xi) = G_c(\Delta\varphi(\xi) + EMF(\xi)) \quad \text{(in coulomb/s = A).} \tag{21f}$$

When the two poles of the battery are connected via a resistance, an electric current can flow. This practically immediately increases ($\Delta\varphi < 0$ becomes more positive) the electrical potential difference coupled to the *EMF*. The former parameter is obtained by equating the current flowing in the battery through the coupled reaction with the current passing through the external resistance (1/Ge),

$$G_c\left(\Delta\varphi + EMF\right) = G_e\left(-\Delta\varphi\right),$$

leading to

$$\Delta\varphi(\xi) = -\frac{G_c}{G_e + G_c}EMF(\xi), \qquad (22a)$$

or with $U(\xi) = -\Delta\varphi(\xi)$,

$$U(\xi) = \frac{G_c}{G_e + G_c}EMF(\xi) \qquad (22b)$$

Setting the coupling conductance to $G_c = 200/6$, and the external conductance to $G_e = 0.42$ $1/\Omega$, yields e.g., $I(0) = 5.287$ A and $U(0) = 12.588$ V.

How the curves of Figure 3 (especially Figure 3(a)) come about can be seen from the behavior at constant EMF. Under such conditions, both curves (3A) would run parallel to the abscissa. Consequently, the decrease of EMF or the increase of $\Delta\varphi$ are solely determined by the changing concentrations of products and reactants (Equation (20c)) [20]. The difference between EMF and $-\Delta\varphi$ values ($-\Delta\varphi < EMF$) is due to the fact that a steady-state-like condition obviously arises for the magnitude of $-\Delta\varphi$. In this process, the inner battery current $G_c\left(\Delta\varphi + EMF\right)$ charges $-\Delta\varphi$ while the outer current $G_e\left(-\Delta\varphi\right)$ discharges it, showing that both conductances are involved.

From Equations (22) also the efficiency of the coupled process can be obtained,

$$\eta = -\frac{\Delta\varphi(\xi)}{EMF(\xi)} = \frac{G_c}{G_e + G_c} = 0.9876, \qquad (23)$$

which does not depend on ξ.

This high efficiency value shows that the discharge reaction is close to equilibrium under these conditions. It therefore seems justified to use the formalism known from non-equilibrium thermodynamics for the reaction flux or the electric current, which is particularly valid close to equilibrium [15] [16].

The output power of the battery is given by,

$$P(\xi) = U(\xi)I(\xi) = G_e\left(\frac{G_c}{G_e + G_c}EMF(\xi)\right)^2 \qquad (24a)$$

$$P(\xi) = G_e\left(\eta\,EMF(\xi)\right)^2, \qquad (24b)$$

and the maximal power is reached, by setting $dP/dG_e = 0$, leading to $G_e = G_c$. Under such conditions, the following values could theoretically be achieved with $G_e = G_c = 33.33$ $1/\Omega$: $\eta = 0.5$, $U(0) = 6.3528$ V, $I(0) = 211.76$ A, and $P_{max}(0) = 1.3453 \times 10^3$ J/s. At the given conductances ($G_c = 33.33$, and $G_e = 0.42$ $1/\Omega$), current and power output are considerably lower, while efficiency is significantly higher. This clearly shows how the velocity of a coupled process affects its power and efficiency. Such a relationship can also be formulated with respect to the irreversibility of a coupled reaction: with

$$1-\eta = \frac{\Delta\varphi(\xi)+EMF(\xi)}{EMF(\xi)} = \frac{T\Delta_{Ri}S_c(\xi)}{EMF(\xi)zF},$$

you get

$$1-\eta = \frac{G_e}{G_c+G_e},$$

and

$$\Delta_{Ri}S_c(\xi) = \left(\frac{G_e}{G_c+G_e}\right)\frac{-\Delta_R G(\xi)}{T}, \tag{25}$$

$$\Delta_{Ri}S(0) = 102.3254\ \text{J}/(\text{mol}\cdot\text{K}).$$

This means that $1-\eta = 0.0124$, or about 1.2% of the coupled process are gone through irreversibly. Power output and entropy production of the coupled reaction are connected by

$$P(\xi) = G_c U(\xi)\frac{T\Delta_{Ri}S_c(\xi)}{zF}.$$

At maximal power output $1-\eta = 0.5$, and $\Delta_{Ri}S_{max}(0) = 4.1117 \times 10^3$ J/(mol·K). If the efficiency approaches one, the power and $\Delta_{Ri}S$ approach zero, so that the reaction can now go through in a virtually reversible manner.

If G_c could be increased, this would lead to a more negative $\Delta\varphi$, and to a larger power output. If $G_c \to \infty$, then $\Delta\varphi \to -EMF$, and thus $\eta \to 1.0$. This could provide a high power output at a high output potential and a comparatively low battery current, so that battery discharge would be slower. However, with the high value for G_c used here, these effects are not very pronounced.

According to Ohm's law, the partial conductances of the coupling conductance G_c, that is, those of $\Delta\varphi$ and *EMF*, respectively, are given by,

$$G_{c1} = \frac{I(\xi)}{\Delta\varphi(\xi)} = G_c\frac{\Delta\varphi(\xi)+EMF(\xi)}{\Delta\varphi(\xi)} = -G_e \quad (G_{c1}<0), \tag{26a}$$

and

$$G_{c2} = \frac{I(\xi)}{EMF(\xi)} = G_c\frac{\Delta\varphi(\xi)+EMF(\xi)}{EMF(\xi)}. \tag{26b}$$

The following must be fulfilled for in series conductances: $G_c = 1/(1/G_{c1}+1/G_{c2})$. Like G_c, both partial conductances do not depend on ξ. Since $U = -\Delta\varphi$, G_e must always be opposite equal to G_{c1}.

The outer current branch of such a circuit can also be understood as an uncoupling of $\Delta\varphi$ through a leak flux.

Despite the use of activity coefficients, the above processes must be considered idealized, since only the one electrochemical reaction Rov has been considered. Other parallel reactions are possible [21] and could influence the results. However, one of the main reasons for the deviation from theoretical behavior during

the discharge process may be caused through the structural changes at the electrodes [21] [22].

2.2.2. Entropy Changes during Discharge

For the whole battery at $T = 298.15$ K the entropy is given by $\Delta_{Re}S = 6\Delta_{Re}S_{SA} = 1.5801 \times 10^3$ J/(mol·K). This means that a lead acid battery would absorb a quantity of heat of $T\Delta_{Re}S = 4.7111 \times 10^5$ J/mol from surroundings by entropy exchange alone, regardless of the reactant concentrations involved. In addition, irreversible heat appears due to the irreversible reaction process during discharge. The closely related dissipation functions are,

$$\Phi_1(\xi) = I(\xi)\Delta\varphi(\xi) = G_c\left(\Delta\varphi(\xi) + EMF(\xi)\right)\Delta\varphi(\xi) \tag{27a}$$

(for the output force $\Delta\varphi(\xi)$),

$$\Phi_1(0) = -66.1244 \text{ J/s},$$

and

$$\Phi_2(\xi) = I(\xi)EMF(\xi) = G_c\left(\Delta\varphi(\xi) + EMF(\xi)\right)EMF(\xi) \tag{27b}$$

(for the input force $EMF(\xi)$),

$$\Phi_2(0) = 66.9576 \text{ J/s}.$$

The dissipation function Φ_1 is opposite equal to the power output P, and for the entire coupled reaction given by

$$\Phi_c(\xi) = \Phi_1(\xi) + \Phi_2(\xi) = G_c\left(\Delta\varphi(\xi) + EMF(\xi)\right)^2, \tag{27c}$$

$$\Phi_c(0) = 0.8332 \text{ J/s}.$$

The entropy production of the coupled reaction is obtained from $\Phi_c(\xi)$ by

$$\Delta_{Ri}S_c(\xi) = \frac{\Phi_c(\xi)}{J(\xi)T}, \tag{27d}$$

$$\Delta_{Ri}S_c(0) = 102.3254 \text{ J/(mol·K)}.$$

If the outer current branch is counted as part of the surroundings, electrical energy becomes dissipated at this location when current flows through this branch via a resistance. This dissipation function is given by

$$\Phi_e(\xi) = I(\xi)U(\xi) = G_c\left(\Delta\varphi(\xi) + EMF(\xi)\right)\left(-\Delta\varphi(\xi)\right) \text{ (with } -\Delta\varphi(\xi) = U(\xi)\text{)},$$

$$\Phi_e(0) = 66.1244 \text{ J/s}.$$

This value must be opposite equal to

$$\Phi_1(\xi) = -\Phi_e(\xi).$$

If dissipation in surroundings were included, with $\Phi_1(\xi) = -\Phi_e(\xi)$, the result would be,

$$\Phi_1(\xi) + \Phi_2(\xi) + \Phi_e(\xi) = \Phi_2(\xi).$$

Unlike the dissipation of the coupled reaction, however, this irreversible heat production is driven solely by an electric potential difference. As a conservative force, it alone is directly responsible for the flow of charges and the generation of heat. This kind of heat and entropy production is given by,

$$\Delta_{Ri}S_e(\xi) = \frac{\Phi_e(\xi)}{J(\xi)T} = \frac{U(\xi)zF}{T},$$

$$\Delta_{Ri}S_e(0) = 8.1211 \times 10^3 \, \text{J}/(\text{mol} \cdot \text{K}).$$

Because $\Phi_1(\xi) = -\Phi_e(\xi)$, this leads also to $\Delta_{Ri}S_1(\xi) = -\Delta_{Ri}S_e(\xi)$, and likewise

$$\Delta_{Ri}S_2(\xi) = \frac{\Phi_2(\xi)}{J(\xi)T}.$$

$\Delta_{Ri}S_1(0) = -8.1211 \times 10^3$, and $\Delta_{Ri}S_2(0) = 8.2234 \times 10^3 \, \text{J}/(\text{mol} \cdot \text{K})$.

The heat absorbed by a battery from surroundings through the coupled reaction is given by,

$$\Delta H(\xi) = \int_0^{\xi} \Delta_R G_c(\xi) d\xi + T \Delta_{Re} S \times \xi, \tag{28}$$

$$\Delta H(2) = -5.8853 \times 10^4 + 94.2214 \times 10^4 = 88.334 \times 10^4 \, \text{J} \, (298.15 \, \text{K}).$$

Thus, for a discharge of e.g. $\xi = 2.0$ mol ($\triangleq t = \frac{1}{3600} \int_0^2 \frac{1}{J(\xi)} d\xi = 21.03 \, \text{h}$),

88.334×10^4 J of heat energy is taken up by the battery. Adding the electrical energy dissipated in surroundings (467.0866×10^4 J), a total amount of heat of $467.0866 \times 10^4 - 88.334 \times 10^4 = 378.7526 \times 10^4$ J appears in this location. This means that during discharge over an external resistance, both the system and the surroundings will heat up.

2.2.3. Electrode Potentials

In the foregoing, the electric potential difference of the overall reaction has been derived from its thermodynamic quantities. However, the total reaction can be divided into two partial reactions, which take place at the anode and cathode, respectively, according to reactions Rox and Rred. The electric potential differences occurring at the electric double layers of the respective electrode can also be determined from the thermodynamic data of these electrochemical partial reactions. For anodic oxidation and cathodic reduction (discharging, $\Delta_R G^0_{SAox} = -68.61 \times 10^3$ J, $\Delta_R G^0_{SAred} = -325.538 \times 10^3$ J) the following equations result,

$$\Delta_R G_{SAox} = \Delta_R G^0_{SAox} + RT \ln\left(\frac{a^2_{H^+}}{a_{H_2SO_4}}\right) = \Delta_R G^0_{SAox} + RT \ln\left(\frac{1}{m\gamma_\pm}\right), \tag{29a}$$

and

$$\Delta_R G_{SAred} = \Delta_R G^0_{SAred} + RT \ln\left(\frac{a^2_{H_2O}}{a_{H_2SO_4} a^2_{H^+}}\right) = \Delta_R G^0_{SAred} + RT \ln\left(\frac{a^2_{H_2O}}{16(m\gamma_\pm)^5}\right), \tag{29b}$$

respectively. The corresponding *EMF* values for a battery are, $EMF_{ox}(0) = 2.1333$, and $EMF_{red}(0) = 10.1219$ V.

Protons generated at the anode migrate to the cathode where they are consumed. The associated charge transport through the electrolyte of the battery thus completes the electric circuit. At higher currents, it cannot be ruled out that an additional electrical potential difference is generated, which is caused by a limited proton mobility and is opposite to $\Delta\varphi$. However, such a mechanism can be neglected if the current is relatively low, as is the case here.

For $\xi = \xi_{st} = 1.0092$, the logarithmic terms of the Gibbs potentials for these partial reactions should also vanish, as has been shown for the overall reaction. For $\xi = \xi_{st}$, the log terms of the Gibbs potentials of both electrode reactions must be zero, leading to $\Delta_R G_{SAox}(\xi_{st}) = \Delta_R G_{SAox}^0$ and $\Delta_R G_{SAred}(\xi_{st}) = \Delta_R G_{SAred}^0$, respectively. However, this requirement is only approximately satisfied, $\Delta_R G_{SAox}(\xi_{st}) = -67.272 \times 10^3$ instead of $\Delta_R G_{SAox}^0 = -68.61 \times 10^3$ J/mol, and $\Delta_R G_{SAred}(\xi_{st}) = -326.876 \times 10^3$ instead of $\Delta_R G_{SAred}^0 = -325.54 \times 10^3$ J/mol. Possibly, the deviations are primarily due to the application of the mean activity coefficient, which, as a geometric mean can only provide an approximation of the single ion activity of H$^+$ ions.

In principle, the same laws apply to the calculation of all thermodynamic functions for both electrode reactions as to the overall reaction. The sum of the values of the partial reactions at the respective electrodes must always be equal to the results for the overall reaction. This gives the values $\Delta_{Re} S_{SAox} = 63.66$ J/(mol·K), and $\Delta_R H_{SAox}^0 = -10.67 \times 10^3$ J/mol for the cathode, and $\Delta_{Re} S_{SAred} = 199.69$ J/(mol·K), and $\Delta_R H_{SAred}^0 = -304.93 \times 10^3$ J/mol for the anode. This means, however, that most of the irreversible heat is produced at the cathode. The respective efficiencies are the same for both electrode reactions and moreover identical to the efficiency of the overall reaction.

2.2.4. Charging of a Discharged by a Charged Battery

The situation changes drastically when the electrical potential difference $-\Delta\varphi$ is not dissipated but transferred into work. For example, this can be done by charging a second, discharged battery. In this case, electrical energy from the fully charged battery is transferred into electrochemical energy of the initially discharged battery. This is achieved by reverse connection of the charged battery I with the discharged battery II. The reaction direction in battery I is maintained (=direction of the spontaneous discharge reaction with H$_2$SO$_4$ consumption), whereas in battery II it is forced into the reverse direction.

$$EMF_{rev}^0 = -EMF^0, \quad \Delta_{Re} S_{SArev} = -\Delta_{Re} S_{SA}, \quad G1_c = 33.3333 \, 1/\Omega, \quad G2_c = G1_c/2 \, 1/\Omega.$$

Battery I starts at an $EMF1(0) = 12.7056$ V, and battery II at an $EMF2_{rev}(0) = -EMF1(2) = -11.7801$ V.

The electrical potential difference of battery II ($\Delta\varphi_{rev} > 0$) is opposite equal to that of battery I ($\Delta\varphi < 0$) virtually immediately. It is obtained by equating the

currents through battery I and II (Figure 3(d)),

$$G1_c \left(\Delta\varphi(\xi) + EMF1(\xi) \right) = G2_c \left(EMF2_{rev}(\xi) + \left(-\Delta\varphi(\xi) \right) \right),$$

(neglecting the resistance of connecting wires),

$$\Delta\varphi(\xi) = \frac{G2_c \, EMF2_{rev}(\xi) - G1_c \, EMF1(\xi)}{G1_c + G2_c}, \tag{30}$$

$$\Delta\varphi(0) = -12.3971 \, \mathrm{V} \,.$$

The current can be expressed by three different formulas that have the same result,

$$I1(\xi) = G1_c \left(\Delta\varphi(\xi) + EMF1(\xi) \right), \quad I1(0) = 10.2836 \, \mathrm{A}, \tag{31a}$$

$$I2(\xi) = G2_c \left(EMF2_{rev}(\xi) + \left(-\Delta\varphi(\xi) \right) \right), \quad I2(0) = 10.2836 \, \mathrm{A}, \tag{31b}$$

and with

$$G12_c = \frac{1}{\dfrac{1}{G1_c} + \dfrac{1}{G2_c}} = 11.1111 \, 1/\Omega, \tag{31c}$$

$$I12(\xi) = G12_c \left(EMF1(\xi) + EMF2_{rev}(\xi) \right), \quad I12(0) = 10.2836 \, \mathrm{A} \,.$$

The Gibbs potential of the overall charging reaction is (Figure 3(d)),

$$\Delta_R G12(\xi) = -zF \left(EMF1(\xi) + EMF2_{rev}(\xi) \right), \tag{32}$$

$$\Delta_R G12(0) = -1.7861 \times 10^5, \text{ and } \Delta_R G12(1) = 0 \, \mathrm{J/mol} \,.$$

Their integrals up to equilibrium at $\xi_{eq} = 1.0$ (see below) are given by

$$\Delta G1_c = \int_0^1 \Delta_R G1_c(\xi) d\xi = -2.9402 \times 10^4 \, \mathrm{J} \,,$$

$$\Delta G2_c = \int_0^1 \Delta_R G2_c(\xi) d\xi = -5.8803 \times 10^4 \, \mathrm{J} \,,$$

and

$$\Delta G12 = \int_0^1 \Delta_R G12(\xi) d\xi = -8.8204 \times 10^4 \, \mathrm{J} \,.$$

Accordingly, the entropy production up to equilibrium is given by,

$$\Delta_i S1_c = \frac{-\Delta G1_c}{T} = 98.613, \quad \Delta_i S2_c = \frac{-\Delta G2_c}{T} = 197.2261,$$

and

$$\Delta_i S12_c = \frac{-\Delta G12}{T} = 295.8391 \, \mathrm{J/K} \,.$$

The entire entropy $\Delta_e S$ of both batteries exchanged with the environment must vanish, since the respective $\Delta_e S$'s of each battery are opposite equal. The

heat appearing in surroundings from both batteries is thus given by—
$T\Delta_i S12(1) = \Delta G12(1) = -8.8204 \times 10^4\,\text{J}$ during about 36 h of charging, which is considerably less than the heat released by only one battery with external dissipation (-378.7526×10^4 J).

Equating the H_2SO_4 concentrations yields,

$$\frac{n1_{SA}^0 - 2\xi}{1.0 + 2\xi M_{H_2O} 10^{-3}} = \frac{n2_{SA}^0 + 2\xi}{1 + 4M_{H_2O} 10^{-3} - 2\xi M_{H_2O} 10^{-3}},$$

leads to

$$\xi_{eq} = 1.0.$$

ξ_{eq} gives that extent of reaction for both batteries, at which the whole system is at equilibrium. Then $EMF1(1) = 12.2594$, $EMF2_{rev}(1) = -12.2594$, and $\Delta\varphi(1) = 12.259348$ V (negative for battery I and positive for battery II). The current decreases nearly linearly from 10.2836 to 0 A. During the process, in battery I 2.0 moles of H_2SO_4 are consumed, whereas in battery II 2.0 moles are produced. At equilibrium both batteries possess the same H_2SO_4 concentration of 3.8609 mol/kg H_2O.

2.2.5. Activated Complexes and Partition Functions

The occurrence of chemical reactions is facilitated by the attainment of a transition state [23] [24]. This is achieved by arranging the reactants of a reaction into complexes while maintaining the stoichiometry in such a way that uptake of energy (activation) they can decompose into products [8]. The partial reactions of a battery take place at the electrodes, namely in their phase boundaries, where electrical double layers are formed with their respective electrical potential difference. The sum of these potential jumps at both electrodes results in the electrical potential difference $\Delta\varphi$ (<0), which can be measured as $U = -\Delta\varphi$ (>0) at the poles. It is assumed that the respective complexes for the partial reactions are also localized in these phase boundaries, for only there can they be affected by both chemical and electrical potentials.

Figure 4 shows how such activated complexes could be constructed. Two dots each between electrons, atoms or groups of atoms mark the bonds in the complex which have become more labile due to energy absorption. At this state, a rearrangement of the bonds of the reactants to those of the products becomes possible. In Figure 4(a), an activated complex as it might occur at the anode is shown. The two electrons from the Pb remain in the solid body of the electrode (negative pole), while the resulting Pb^{2+} ion can combine with the SO_4^{2-} ion to form $PbSO_4$ after H_2SO_4 has dissociated two protons. In Figure 4(b), such an activated complex at the cathode is shown. Here, two electrons are taken up by the Pb^{IV+} of the PbO_2 of the cathode to form $PbSO_4$ with the SO_4^{2-} ion of the H_2SO_4 molecule. Two protons dissociated from this latter compound, together with two additional H^+ ions of the electrolyte form two H_2O with the residual O_2^{IV-}. The same complexes can obviously also be formed from the products, so

$$\text{Pb} + \text{H}_2\text{SO}_4 \rightleftarrows 2\text{e}^- \cdot\cdot \text{Pb}^{2+} \cdot\cdot \text{SO}_4^{2-} \cdot\cdot 2\text{H}^+ \rightarrow \text{PbSO}_4 + 2\text{H}^+ + 2\text{e}^-$$

(a)

$$\text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \rightleftarrows \begin{array}{c} 2\text{e}^- \cdot\cdot \text{Pb}^{\text{IV}+} \cdot\cdot \text{O}_2^{\text{IV}-} \cdot\cdot 2\text{H}^+ \\ \cdot\cdot \qquad \cdot\cdot \\ \text{SO}_4^{2-} \cdot\cdot 2\text{H}^+ \end{array} \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$$
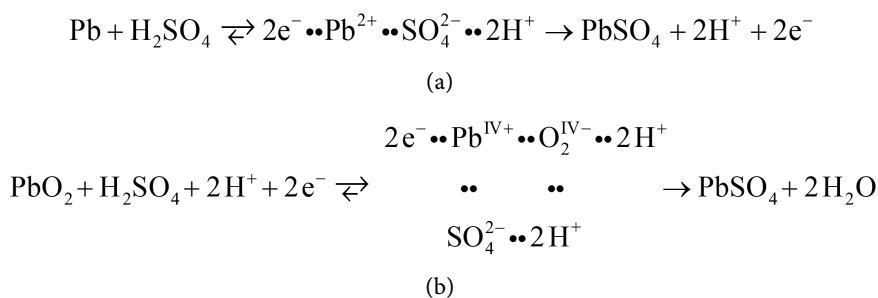
(b)

Figure 4. Configuration of activated complexes. (a): at the phase boundary between anode and electrolyte, Pb²⁺ ions are released from the anode, whereas electrons remain on the electrode surface. (b): at the phase boundary between cathode and electrolyte, electrons are released from the cathode.

that the reaction can also proceed in the reverse direction. Since the reaction is coupled to the formation of $\Delta\varphi$, a simple way to reverse it is to change this quantity accordingly.

The two different electrode reactions occur in the respective electrical double layers, their $\Delta_R G$ values must both be negative. This means that the respective entropy production also takes place at these locations and each must be positive.

For the occurrence of entropy changes during a chemical or biochemical reaction, it is important to understand the energetic processes involved in the formation of transition states from reactants and their decomposition into products. That the equilibrium constant of a chemical or biochemical reaction can also be calculated using Maxwell-Boltzmann statistics and partition functions has been adequately demonstrated [3] [4] [5] [6]. Here, an attempt is made to explain the reactions occurring under non-equilibrium conditions, via the formation of activatable complexes, their activation, and their decay to products. It is assumed that also under these non-equilibrium conditions the Maxwell-Boltzmann statistics (constant energies and particle numbers), which is valid for equilibria, might be significantly involved.

The association reaction of reactants to form complexes that can absorb energy to form transiently activated complexes is assumed to be in an equilibrium-like state ($\Delta_R G_{ass} = 0$). Since no heat energy can arise in this first reaction step, the entire energy of the reactants must have been transferred to the resulting complexes, as would be the case in an at-equilibrium reaction. Activation raises the Gibbs potential of the complexes by $\Delta_R G^{\ddagger}$ ("‡" denotes the activated state). This transiently transforms it to an unstable state, whereby the Gibbs potential of the subsequent reaction step, $\Delta_R G_{diss}$, becomes more negative. After the decomposition of the activated complexes, their activation energy $\Delta_R G^{\ddagger}$ is released again (the same is true for the entropy changes associated with the transition state and activation), so the energy of the reactants first remains associated with the newly formed product molecules. Obviously, however, the energy distribution obtained in this way does not have the maximum possible probability. This might be achieved (constant temperature), when a certain amount of that

energy could be released as heat from the system into the surroundings. This amount is now apparently given by that fraction of energy which corresponds to the difference of the mean particle energies between newly formed products and already present products. This would mean that at an infinitesimal extent of reaction, reactants with the average energy of the remaining reactants in thermal equilibrium enter the reaction and appear as products with just this reactant energy. By releasing this surplus energy as heat energy, their energy is then brought to the mean energy of the products already present, which are also already in thermal equilibrium. In this way, all particles in the system and the environment could remain in or at least close to thermal equilibrium despite an irreversibly extending reaction, thus maintaining the respective energy distributions close to maximum probability.

The corresponding energetic and entropic changes will be explained by means of the following numerical example for the PCr reaction. The reaction proceeds irreversibly starting from the initial concentrations up to equilibrium (see reference [8]). Let the initial concentrations be $[PCr_0]$ = 1.2, $[ADP_0]$ = 1.2, $[ATP_0]$ = 0.8, and $[Cr_0]$ = 0.8 mmol/L. Equilibrium is reached when the reaction has irreversibly extended by ξ_{eq} = 1.06053×10^{-3} mol. This creates a ΔG value of -9.4572 J. With $\Delta_{Re}S$ = 10.2589 J/(mol·K), and $\Delta_e S = \Delta_{Re}S \times \xi_{eq}$ = 0.0109 J/K, you get $T\Delta_e S$ = 3.2485 J and ΔH = -6.2133 J [8].

Initially, 9.4572 J of (integrated) surplus energies are produced in the system, of which in this case ($\Delta_{Re}S > 0$) 3.2485 J must be transferred to the newly formed products to balance the internal energy difference between product and reactant molecules. The remaining energy that can be released by the system as heat is thus given by $9.4572 - 3.2485 = 6.2133$ J. Finally, since this amount of energy is released from the system into surroundings, all signs have to be reversed. This then leads to $\Delta H = \Delta G + T\Delta_e S$ = $-9.4572 + 3.2485 = -6.2133$ J, which matches the known relation, $\Delta G = \Delta H - T\Delta_e S$. The same result would be obtained if the equalization of the intramolecular energies between products and reactants (3.2485 J) were to take place after the release of the total energy difference (-9.4572 J). Such a description would express the associated entropy exchange more clearly, especially in the case that $\Delta_{Re}S < 0$.

For the reverse reaction, initial concentrations are: $[PCr_0]$ = 0.1, $[ADP_0]$ = 0.1, $[ATP_0]$ = 4.0, and $[Cr_0]$ = 4.0 mmol/L. Equilibrium for the reverse reaction is reached when the reaction now has irreversibly extended by ξ_{rev}^{eq} = 0.185846×10^{-3} mol. This creates a ΔG value of ΔG_{rev} = -0.4228 J. With $\Delta_{Re}S_{rev}$ = -10.2589 J/(mol·K) and $\Delta_e S_{rev} = \Delta_{Re}S_{rev} \times \xi_{rev}^{eq}$ = -0.001907 J/K, you get $T\Delta_e S_{rev}$ = -0.5684 J. The total heat for the reverse reaction then is given by, $\Delta H_{rev} = -0.4228 - 0.5685 = -0.9913$ J. Since in this case $\Delta_{Re}S_{rev}$ is negative, the newly formed product molecules this time contain too much intra-molecular energy compared to the reactants, so that additional heat energy has to be released to maintain a constant temperature. Also for the reverse reaction $\Delta G_{rev} = \Delta H_{rev} - T\Delta_e S_{rev}$ is fulfilled.

As the reaction proceeds, the number of product particles increases and the number of reactant particles decreases. The same applies to their energies, but without changing their average energies. In the course of the reaction, a certain point may be reached, where there are no more energy differences between products and reactants, so that $\Delta_R G$ vanishes. Under such conditions, the same activatable complexes can be formed from both the forward reaction from reactants and the reverse reaction from products. Since $\Delta_R G = 0$, no irreversible heat can be generated under these equilibrium conditions and thus also no $\Delta_{Ri} S$ can be produced, the reaction must come to a halt. However, in order to achieve a complete equilibrium at the given temperature, the following condition must also be fulfilled: All particle energies must be distributed according to their respective partition function. Then and only then the system is also in thermal equilibrium.

For the spontaneous progression of a chemical reaction at constant temperature, the following can therefore be stated: As a precondition, there must be a negative energy difference between products and reactants. This actual energy difference, which depends on the reaction extent, is released into the surroundings as heat energy in order to enable an energy distribution of maximal probability between all particles of the system and surroundings.

In case the system boundaries do not allow heat transfer, the system would have to absorb the surplus of energy. This would be considerably more complex and presumably more time-consuming, since all particle species of the system—not just the reaction participants—would have to redistribute onto partition functions that were changed as a result of the temperature shift. This is also known to be associated with a shift in all thermodynamic parameters such as $\Delta_R G^0$.

In non-coupled reactions, the entire Gibbs potential available as $\Delta_R G$ is always converted into heat energy, whereas in a coupled reaction such as the discharge reaction of a battery, part of that input potential can be converted into an electrical potential, so that only the remainder of the input can be released as heat. As shown above, the extent of this transformation is determined by the efficiency, which in turn is essentially determined (for a given Lc) by the conductance Le of the outer current branch. It is hence the magnitude of the current that controls the efficiency of the coupled reaction in a battery. Since the coupling presumably occurs at the phase boundaries of the electrodes, it seems plausible to assume that as current I increases and efficiency η decreases, the charge transport against the respective electrode potentials ($\Delta\varphi_{ox}$ and $\Delta\varphi_{red}$) may be affected first. Apparently, the electrical potential difference $\Delta\varphi$ (counter potential) is used up so quickly that only a reduced (less negative) $\Delta\varphi$ is available for transformation. The rest of the input potential is released as heat. This behavior can also be taken from Equations (27c) and (27d) for dissipation and entropy production (dependence on counter potential $\Delta\varphi$ and hence also on G_e).

It should be noted that this kind of variable entropy production does not arise

from uncoupling. Uncoupling is present whenever an additional leak flux occurs that is driven separately by only one of the potentials, *EMF* or $\Delta\varphi$. For example, if the reaction occurred without charge transport, or if charge could flow back into the direction of the electric field without participation of the reaction. In both cases, additional irreversible heat and entropy would be produced, and the efficiency would be reduced.

The mechanism of such a power enhancement is demonstrated particularly impressively by the reactions leading to the activation of muscle contraction [25] [26]. There is a nerve impulse and a depolarization of the membrane potential at the beginning of this process, which causes the Ca^{2+} concentration in the sarcosol of a skeletal muscle cell to increase drastically. This in turn triggers the contraction process coupled to adenosine triphosphate (ATP) splitting. Under resting conditions, this reaction is far from equilibrium ($\Delta_R G_c \ll 0$) despite coupling, but in an inhibited state. When de-inhibited (activation by [Ca^{2+}]), sufficient power can be released due to this status. The Gibbs potential of ATP splitting becomes more positive as a result, so that the coupled reactions of ATP formation can go through faster. Ultimately, this also includes the metabolism of the fuel glucose. This metabolic pathway is mainly activated at just one point, the phosphofructokinase reaction, by increasing the adenosine monophosphate concentration. Special activation of the many other enzyme-catalyzed reactions involved is apparently not necessary [25] [26] [27]. Obviously, it is sufficient that the counter potentials of a few coupled in-series reactions become less negative, as has been shown for the coupled battery reaction, to also bring about the required increase in power output of the entire energy metabolism of the muscle fiber.

2.2.6. Comparison of Entropy Changes

The amount of entropy $\Delta_e S$ exchanged with the surroundings during volume work depends on whether the process has been conducted reversibly or irreversibly. Under partially irreversible conditions, only a fraction of the maximum that can be achieved under reversible conditions can be exchanged. As has been shown, such a work process can be divided into a completely reversible and completely irreversible part. Only the reversible part is associated with a corresponding $\Delta_e S$. The rest of the volume change is work-free and is associated with entropy production $\Delta_i S$.

Since the work-free volume change is always positive (also under conditions of compression), $\Delta_i S$ must also be positive. Moreover, there is no simultaneous entropy change of the opposite sign at another location, as is the case with the exchanged entropy. Since under reversible as well as partially irreversible conditions the same total volume change occurs (under adiabatic conditions, a reversible and $\Delta_e S$-associated volume change does not exist), which equals the sum of volume changes of the partial processes, the entropies of the partial processes, $\Delta_e S$ and $\Delta_i S$, must also add up to the total entropy ΔS. Thus,

$\Delta S = \Delta_e S + \Delta_i S$, and hence ΔS must equal $\Delta_e S$ under entirely reversible conditions.

Such behavior, on the other hand, is not observed in a partially irreversible reaction such as the discharge of a lead-acid battery. $\Delta_{Re} S$ as well as $\Delta_e S$ do not depend on whether the reaction has gone through reversibly or irreversibly. Consequently, there can be no interrelation between $\Delta_{Re} S$ and $\Delta_{Ri} S$ (or $\Delta_e S$ and $\Delta_i S$ of a reaction), like the entropy summation in the case of volume work. For chemical and biochemical reactions, $\Delta_{Re} S$ is temperature-dependent and, like $\Delta_R G^0$, changes its sign when the direction of the reaction becomes reversed.

However, entropy changes during volume work and reactions exhibit an identical behavior in two essential points. In both processes, entropy production is associated with an increase of the process velocity and thus, also with an increase (up to a maximum value) of its power output. This is as if a real force were causing an acceleration. However, there is no such force. The higher process speed by entropy production is due to the tendency to maximize the probability of energy distribution at the molecular level. Secondly, both processes produce additional heat in the surroundings under partially irreversible conditions and at constant temperatures. In the partially irreversible Carnot cycle, this is caused by the occurrence of free expansions, which can arise as a result of rapid piston movement. This means that more heat energy remains in the surroundings during the expansion process, while more heat energy is released into the surroundings during the compression process (Table 1 and Table 2). This releases more $\Delta_e S$ into the surroundings, but also produces a corresponding amount of $\Delta_i S$ (Table 2). In chemical reactions, the surplus energy of the reactants, which has not been transformed by coupling, is responsible for that additional heat in the surroundings. In this case, it is accompanied by a corresponding $\Delta_i S$ but not by a further change in $\Delta_e S$.

2.3. Reaction Coupling in Biological Systems

In living cells, many reactions are only possible through coupling. These include all synthetic reactions such as protein biosynthesis, and a number of ion transport reactions such as the Na/K pump and the Ca pump. In this context, special mention should be made of muscle contraction, in which mechanical work is obtained from the chemical energy of ATP splitting through coupling.

The coupling phenomena occurring in living cells are known to be far more complex than the association of reactants to activatable complexes in a non-coupled, completely irreversible reaction or the coupling via electrical potential differences of electrodes in a partially irreversible reaction. For example, in order to couple proton transport across the inner mitochondrial membrane to ATP synthesis via ATP synthase, the cell must be equipped with highly differentiated protein complexes that fulfill this task as molecular machines, so to speak. The energetic and entropic principles of the coupled reaction itself remain the same,

however.

The entire energy metabolism of a cell such as the muscle cell can be viewed as the flow of energy coupled to ATP formation, which in turn through ATP splitting is coupled to work functions such as ion transport, contraction, or biochemical synthesis. This is comparable to a battery whose external current branch is connected to another battery or, for instance, to an electric motor. The electrical potential difference corresponds to the $\Delta_R G$ of ATP formation (positive), whereas the work of the electric motor can be assigned to the work functions specified above.

Power generation in the course of energy transformations is achieved by the process of energetic coupling, as has been demonstrated here for processes as different as volume work and chemical reactions. It is of the most significant importance, both in technology and also in the living cell. In this context, it is imperative that the input energy is not only available in sufficient quantity, but that this energy or the potential associated with it can also be transformed at the required speed by coupling. From this, it can be concluded that the coupling mechanism should particularly have a high coupling conductance (L_c). It follows, though, that both the performance of man-made machines and the viability of cells depend not only on energy, but to no less significant an extent on the ability to produce entropy.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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