"Ueber einen allgemeinen qualitativen Satz für Zustandsänderungen nebst einigen sich anschliessenden Bermekungen, insbesondere über nicht eindeutige Systeme," Ann. Phys. (Leipzig) 33 (1888), 337-353.

# On a general qualitative theorem for state changes, along with some related remarks, in particular, on non-unique systems ${ }^{(1)}$ 

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Translated by D. H. Delphenich

1.     - Let the state of a system be determined uniquely by certain of its quantities. Let it be in stable equilibrium for well-defined values of the variables, and let it be possible for the system to run through a series of stable equilibrium states continuously by continuously changing those variables, i.e., in such a way that, in general, an infinitely-small change in one of the variables will be coupled with only an infinitely-small change in all of the other quantities that occur in the system. Furthermore, let a finite change in one of the variables be coupled with finite changes in those quantities that should change simultaneously with the first (independent) variables, at least in special cases. If one starts from one of those equilibrium states and changes one of the variables by a very small quantity then a new equilibrium state will be established. Now, there are two different types of systems to distinguish.
A. First class of systems. - These are the ones for which a finite time can elapse until the other variables have changed, in such a way that it arrives at the new equilibrium state. We shall first speak of these. If one has produced an infinitely-small change in one of the variables arbitrarily and then waits for the changes in the variables to occur as a result of the transition to the new equilibrium position then obviously those changes in value cannot grow beyond a finite quantity. Otherwise, by assumption, that change would also require a finite change in the former variables, and it would not be possible at all to establish a state that is infinitely close to the initial state, which would contradict the assumed continuity. Let $x, y, \ldots, t$ be the variables in an initial equilibrium state. One keeps all of them constant except two - e.g., $x$ and $y$ - while $x$ changes arbitrarily by the very small quantity $+\xi$ and then waits for the new equilibrium state to be established. When it has been established, $x$ and $y$ change by $\partial \xi$ and $\partial y$, resp., and it can always be arranged that $\partial \xi / \partial y$ has a unique finite value (e.g., by defining a solution, when $x$ is, say, the pressure and $y$ is the volume of the solution, when one imagines that the newly-defined layer of

[^0]the solution is always distributed uniformly in the entire fluid that is present). Let a change in $\xi$ that occurs by itself be denoted by:
$$
\delta \xi=\delta x=\frac{\partial \xi}{\partial y} \delta y
$$

I would like to prove that $\delta \xi$ must always have the opposite sign to $\xi . \delta \xi$ and $\xi$ will then have equal orders of magnitude, which would follow from the assumption.

Let $\delta y$ be assumed to be positive. Now, if $\partial \xi / \partial y$ were also positive and constant then the $+\xi$ that is produced arbitrarily would go to $+(\xi+\delta \xi)$, and since, on the other hand, $(\partial y / \partial \xi) \delta \xi$ would also be a positive constant, the changes in the variables would attain finite values by themselves. As a result, only the following assumptions will remain:
a) Either $\partial \xi / \partial y$ is not constant, but already converges to zero for an infinitely-small interval $d y$, which would contradict the assumed continuity,
b) $\operatorname{Or} \partial \xi / \partial y=0$. This case (viz., indifferent equilibrium) is excluded by assumption, i.e.,
c) The only possibility that remains is that $\partial \xi / \partial y$ is negative. It then follows that $\delta \xi$ must be negative when $\xi$ is positive, and conversely, independently of the sign of $\delta y$, as one easily convinces oneself by repeating the proof. In words: If the arbitrarily-produced change in one of the variables is $+\xi$ and the change that occurs by itself in the other is $\pm \delta y$ then the change that occurs by itself in the first variable will be - $\delta x$, i.e., the transition to the new equilibrium state will always be such that the absolute value of the arbitrarily-produced change in one of the variables that causes the transition will decrease by itself under that transition.

A continuously-stable varying system is then, at the same time, a self-relaxing one. I would like to call it autostatic (which is short for the more correct term "auto-ephistatic").

Thus, the assumption is that the system will be left alone under the transition. Therefore, if the temperature is a varying quantity then the change must be thought of as adiabatic.
2. That theorem subsumes the qualitative aspects of a great number of known phenomena, and it is suitable for producing new ones. I would like to apply the theorem to several of them: Let the given system be ice and water at $0^{\circ}$. If one raises the pressure by $d p$ (the temperature remains constant), so one produces an arbitrary change in the volume $-d v$, then a change in volume $+\delta v$ must occur by itself (and a change in pressure $-\delta p$ ). Since ice has a greater specific volume than water, ice must partially melt. The opposite is true for substances that expand under melting. The influence of pressure on the solubility of solid bodies in fluids falls within the scope of the same argument. Substances that by dissolve better under increasing pressure must contract under that
pressure; the ones that dilate under solution must precipitate under increasing pressure ( ${ }^{1}$ ). The same thing is obviously true for fluids that are immiscible in any ratio.

I would like to apply the theorem to the case of adiabatic changes. Let a saturated solution of salt be in contact with salt itself. If one raises the temperature by $d t$ and lets the new equilibrium state come about then if new salt is to enter into solution then that would absorb heat, and the same thing must be true when salt precipitates, i.e., substances whose solubility increases with temperature will absorb heat when they enter into the almost-saturated solution (viz., negative heat of solution), while the ones whose solubility decreases will dissolve with a release of heat. (The quantities $\lambda$ and $\eta$ in my previously-cited treatise are always of opposite sign then. The sign of $\varepsilon$ is determined by only that of $v).\left({ }^{2}\right)$

I regarded this theorem as new when I wrote the notice in Zeit. phys. Chem that was mentioned to begin with. Only later, after a more detailed perusal of the literature, did I see that it had been expressed by Le Châtelier [C. R. Acad. Sci. Paris 99 (1884), pp. 788]. It immediately become the topic of a debate among French scholars. I do not know whether Le Châtelier, who indeed also examined [C. R. Acad. Sci. Paris 104 (1887), pp. 679] the heat of formation of a saturated solution (but of salt and water), specified it in the ways that I did above, namely, that it relates to only the effects of heat when one enters an already almost-saturated solution. In the cited paper in 1884, as I found on that occasion, Le Châtelier presented a theorem for "systems in stable chemical equilibrium" that read almost the same as the one that I expressed. However, I found neither a sharp boundary on the conditions for its validity nor a proof of it, and therefore with an almost identical wording, the implications that Le Châtelier attached to his theorem would be completely different. That is best illuminated by the applications that Le Châtelier gave. Most examples are of a chemical nature. By contrast, the theorem must also include the radiation of heat from a strongly-heated location, the transport of metal from a point on a strip that is immersed in a solution of a salt of the metal to another point, and the lowering of the melting point of an alloy or a mixture of salts during progressive solidification. A precise formulation (likewise without proof) can be found in Ostwald (Allg. Chem., v. 2, pp. 736). However, not all of the examples that are cited there are applicable.

The potential difference between the poles of a chain (Kette) is coupled with just its temperature. If one raises the latter and a change in the potential difference arises in that way, i.e., a charge current, then conversely, the charge current must cause a decrease in temperature for the cell, i.e., if it has the same direction as the original current in the cable (increasing electromotive force with increasing temperature) then the cable must be cooled by such a current. The opposite will happen when the electromotive force decreases with increasing temperature. That is the qualitative significance of von Helmholtz's theorem $\left({ }^{3}\right)$. The temperature change in unequallyheated metallic conductors results in entirely the same way (viz., the Peltier and Thomson effects). If one imagines that the two plates of a condenser that consists of two different metals are heated,

[^1]along with the connecting wires (without changing the capacity), then the charge current that arises in that way will correspond to the thermoelectric force on the soldering points, while the heat that the system develops or absorbs will correspond to the Peltier heat. Now, if only the contact points are heated, but the temperature of the condenser plates is left unchanged, then the charge will correspond to the thermoelectric forces on the solder points, and the charge that appears inside of the metals of the same type will correspond to the heat of the Peltier and Thomson effect. Since the two of them can be separated when the thermoelectric force is known as a function of temperature, experiments of that kind might lead to a resolution of the question of whether the changes that the contact electricity experiences with temperature depend upon only the metals that are in contact or also upon the intermediary of the condenser.

However, the following example might serve to show that the theorem must be applied only with caution: It is known that in hemimorphic crystals an electric charge with a certain potential difference must arise from a change in pressure, and conversely, a pressure difference must arise from an electric charge. Both of them are coupled with each other in such a way that when a potential difference $+p$ in a fixed direction results from a pressure increase, a charge $+p$ of that kind will, conversely, produce a pressure decrease. One might then seek to also deduce that phenomenon from the theorem. However, that is admissible only when it has been proved that pressure and charge are uniquely coupled to each other, i.e., that when one quantity changes, the other one can also take on only a single value in the new equilibrium state. The theorem would then be applicable if it had been proved that a plate of a hemimorphic crystal that was cut in a suitable direction (and perhaps provided with occupancies [Belegungen]) would admit only a single, generally non-zero, value of the potential difference in it as an equilibrium state. That condition would be fulfilled by the aforementioned examples, and since probably all solid bodies are conductors of electricity, it will probably also be valid for them. As Riecke ( ${ }^{1}$ ) has recently shown, when one is careful to isolate it sufficiently, any hemimorphic crystal will take on a welldefined continuing electrification for a given temperature, so the theorem can be applied to that phenomenon and its reciprocal.

It will then be applicable to, e.g., the following case: If the electromotive force on a galvanic element is changed by pressure, i.e., a charge current is produced, then, conversely, that will bring about processes that cause a decrease in volume $\left(^{2}\right)$. That conclusion was already inferred in a different way.

Even when a change in the electric voltage difference arises in metallic conductors by a rise in pressure (reduction of volume), conversely, such a charge current must cause an increase in volume. One could hardly doubt that the former is the case. The properties of continuallyhardening metals must continually go over to the ones in metals in the natural state through those temporarily-denser ones (as it occurs in, say, the solidification of melted materials or in electrolytic

[^2]deposition). If one would also like to assume that two metals of the same chemical composition in different physical states will possess no electric voltage difference at one temperature then that would no longer be true for another one, since it is known that this will produce thermal currents. It follows from this that: If one raises the pressure in a condenser that consists of two different metal plates (without changing the capacity) to its full value then the charge will change. The same thing will happen when one subjects one of two equal metal plates to pressure forces. The closer that one brings the plates from the outset (i.e., the greater the capacity), the greater that the amount of moving electricity will be. Even when they contact (i.e., the loop is closed), a current must still arise. However, from the inverse relationship, the resistance of the contact location of the plate would distribute to the resistance of the remaining conductor between the two open paths. That current cannot be permanent, since its equivalent can be sought only in external work, and such a thing cannot be supplied continually as a result of the conditions of the experiments. It can then appear only temporarily (as a charge current). However, when such a current arises by pressure changes in metals (i.e., by the rapid changes of volume that they produce), there will be grounds for saying that any such change of volume should not be accompanied by such a thing. That situation can enter into play in the excitation of momentary currents that arise when one brings a hot metal together with a cold one.

Finally, I would like to refer to a case that is quite interesting at the moment. It was verified by known experiments that the resistance of many metals changes in a magnetic field. In particular, Goldhammer $\left.{ }^{( }{ }^{1}\right)$ extended the results of other researchers and arrived at the conclusion that the resistance of all metals increases in the direction of magnetic force lines (to the extent that the change is observable at all). In the direction that is perpendicular to it, it increases only in diamagnetic metals; in magnetic ones, it decreases. One then imagines the following experimental arrangement: A constant electromotive force sends a current through a solenoid and a number of metal wires that are found in the magnetic field of the solenoid. Let all of the wires be of the same material, and let the entire arrangement be kept at constant temperature. If one displaces the wires from locations of lower magnetic field strengths to locations of greater ones then the current strength will change. For the diamagnetic metals, from the results of experiments, the system will obviously always be an autostatic one. Displacements to locations of stronger magnetic forces will cause a reduction in current strength, i.e., a reduction in field intensity. For magnetic metals, however, one can exhibit conditions under which the opposite situation would occur, from the cited observations. Hence, when the system is also an autostatic one in this case (and I see no reason to say otherwise), a new effect must be present. If one wonders what sort of changes would be possible then it seems to me that only one assumption still remains, namely, that the resistance of magnetizable metals must increase with increasing field strengths. Since that change occurs in the same sense as is required by the increasing Joule heating, it would not be entirely easy to verify such a small change beyond dispute.
B) A second class of systems is defined by the ones for which it is not possible to change a variable without changing at least one other variable simultaneously. In many cases, one might be able to show that they differ from the former category only by the magnitude of the time interval.
${ }^{(1)}$ Goldhammer, Wied. Ann. 31 (1887), pp. 360.

For example, the pressure that acts upon a rigid body can be changed suddenly while its volume can be regarded as unchanged during the first moment. However, as long as one considers the ordinary mechanical properties of that body (e.g., relations between volume and pressure, tension and length, etc.), the theorem above will not give anything that was not expressed already by the simplest basic laws of mechanics. It proves to be fruitful only when one either includes other properties (like magnetization) or when one lets the temperature be variable. However, that system can then be treated similarly to one of the first class. It then follows that, e.g.: If one imagines that a body that is exposed to a pressure $p$ at the onset is heated by $+d t$, but its volume is kept constant (such that $p$ goes to $p^{\prime}$ ), then $d t$ must always decrease, i.e., cooling must occur. That is because, by assumption, $d t$ must experience a change, since it should vary with a change in volume. However, if it were to increase due to the possibility of free change of volume that is now given then the latter would go further in the sense of increasing temperature, which would again change the temperature in the same sense, so precisely the conclusion that was reached in § $\mathbf{1}$ would again be valid. Hence, bodies that expand under heating ( $p^{\prime}>p$ ) will cool under adiabatic expansion. Ones that contract ( $p^{\prime}<p$ ) will cool under adiabatic contraction, i.e., they will heat up under adiabatic expansion. If the total (but very small) change in $p$ during that process (so $p-p^{\prime}$ ) is denoted by $\partial p$ and the associated change in temperature by $\partial t$ then $\partial p / \partial t$ will have a well-defined numerical value, while it will not remain the same during the tumultuous process.
3. - Complications will arise when the system is not unique. That would be the case in the example that was just mentioned as soon as permanent deformations or elastic aftereffects assert themselves. The qualitative law will also remain valid as long as the differential quotients of the variables keep the same signs that they have in the analogously-defined unique system (so an ideal elastic body here). If one connects the considerations to such an ideal case then one can also infer in which direction the deviations from the ideal case must lie for the real case. I would like to work that out in the cited example (thermal effect of lengthening of a wire). Let the differentials be given by uppercase symbols for the ideal case and by lowercase symbols for the real case. One will then have:

$$
\Delta t=\frac{D t}{D p} \Delta p, \quad \delta t=\frac{\partial t}{\partial p} \delta p
$$

If one makes $\Delta p=\delta p$ then:

$$
\frac{\Delta t}{\delta t}=\frac{D t / D p}{\partial t / \partial p}
$$

$D t$ corresponds to a certain value of $D p$. That will no longer be true for the relations between $\partial t$ and $\partial p$. However, one observes that:

$$
\partial t / \partial p=\frac{\partial t / \partial v}{\partial p / \partial v}
$$

so from the properties of the elastic aftereffect, one will have $\partial t / \partial v=D t / D v$, at least very nearly $\left(^{1}\right.$ ); by contrast, $\partial p / \partial v<D p / D v$. Therefore, if $\alpha$ denotes a proper fraction that is defined by $\partial p / \partial v=\alpha D p / D v$ then one will have $(D t / D p) /(\partial t / \partial p)=\alpha \Delta t / \delta t$ or $\delta t=1 / \alpha \Delta t$, i.e., the adiabatic temperature change for a yielding body is greater than the one for the ideal elastic body that is calculated in thermodynamics.

That behavior is actually expressed in Joule's results in regard to the situation. In order to prove that, I shall exhibit the numbers $\left({ }^{2}\right)$ :

|  | Experiment |  | Theory |  |
| :---: | :---: | :---: | :---: | :---: |
| Iron. | -0.115 | ${ }^{\circ} \mathrm{C}$ | -0.110 | ${ }^{\circ} \mathrm{C}$ |
| " | -0.124 | " | -0.110 | " |
| " ............... | -0.101 | " | -0.107 | " |
| Hardened steel.. | -0.162 | " | -0.125 | " |
| Cast iron.. | -0.160 | " | -0.112 | " |
| Copper........... | -0.174 | " | -0.154 | " |
| Brass............ | -0.053 | " | -0.040 | " |
| " ............... | -0.076 | " | -0.055 | " |
| Gutta percha.... | -0.028 | " | -0.031 | " |
| " ............... | -0.052 | " | -0.066 | " |

Joule did not regard the experimental numbers that were given for gutta percha as reliable $\left(^{3}\right)$. The same thing is true to an even greater degree for the effect that was found for wood $\left({ }^{4}\right)$, to which Joule attached a correction of $25 \%$ of the directly-observed numbers. For that reason, I shall skip over that example, but remark that Joule gave smaller values than the theory would demand in the three cases considered (which is the opposite of the behavior of metals).
4. - It seems to me that the same conclusion is not allowed from the considerations of the mechanical theory of heat. As long as the conditions of reversibility are no longer fulfilled, the justification for the calculations in the usual form also breaks down, and one must follow a process that is defined in complete analogy with that of Carnot in order to arrive at reliable conclusions. If one constructs such a thing that is bounded by two isotherms $T$ and $T^{\prime}$ and two adiabats then one will initially have:

$$
Q-Q^{\prime}=\mu\left(T-T^{\prime}\right)=\frac{1}{J} F_{1}
$$

for the ideal case, when $F_{1}$ means the work done on the system from the outside, $T>T^{\prime}$, and $J, Q$, $Q^{\prime}$ have the known meanings. If one now takes the real case (as one could already get from the ideal case by extending the time interval) then one can always arrange that the same amount of

[^3]heat will be absorbed (emitted, resp.) as in the ideal case at the same temperature. The transition from $T$ to $T^{\prime}$ will also be possible along an adiabat. However, if one would like to return the body from $T^{\prime}$ to its initial state $(p, v, T)$ along an adiabat then it would certainly not have the initial value of $v$ for the initial $p$, and most likely, not the initial value of $T$, either. The entire form of the work surface will have changed with respect to the ideal case, and what one can initially conclude is only that the external work done on the system $F_{3}$ is less than $F_{1}$. Therefore, one has:
$$
J\left(Q-Q^{\prime}\right)=F_{2}+U
$$
in which $U$ means an internal energy that remains in the body. If only elastic aftereffects occur, i.e., if the body returns to its initial state, if only after a very long time [in which it is assumed that when it reaches the same length that it had to begin with, its internal energy will again be the one that it had in the initial state, which is not generally true, as is shown in the superimposition of reactions $\left({ }^{1}\right)$ ], and one imagines that it is adiabatically enveloped during that entire time then the total external work must also be the same as in the first case. The total amount of $U$ is then converted into external work. However, it is still initially undecided whether that happens, since the wire cools, or whether $U$ is not (at least, for the most part) an internal potential energy (of position) that is equivalent to freely-convertible work, which is what I consider to be most likely. A resolution by direct experiment seems out of the question. Indirectly, there is the possibility that a metal that is found in a state of elastic aftereffect must be electromotively effective in comparison to the same thing in the ordinary state in a solution of a salt of the metal in question. Indeed, the one that is found in the state of reaction must be the negative pole of the element, because when that metal is dissolved in a closed current loop that is presented in that way and deposited on the other electrode in the ordinary state, that capacity to do internal mechanical work would be converted into the electrical energy of the current loop. If $U$ denotes the internal work that is stored as elastic aftereffect in an amount of metal that is electrochemically equivalent to 2 g of hydrogen, which is expressed by the product of stress and the elongation by aftereffect, and $J U$ is its equivalent amount of heat in gram-calories then the electromotive force $e$ that relates to Daniell $=$ 100 will be $\left(^{2}\right)$ :
$$
e=\frac{1}{500} \cdot \frac{U}{J}=\frac{1}{500} \cdot \frac{U}{41.6 \cdot 10^{6}},
$$
approximately, or when one assumes that the electrochemical unit of electricity is equal to 193,000 Coulombs:
$$
e=\frac{U}{193} \cdot 10^{-10} \text { Volt }
$$
and $U$ itself will become:
$$
U=\frac{A \cdot P \cdot v}{m} \cdot 1000 \cdot 981 \quad\left[\mathrm{G} \mathrm{C}^{2} \mathrm{~S}^{-2}\right]
$$
${ }^{(1)}$ F. Kohlrausch, Pogg. Ann. 158 (1876), pp. 372.
$\left(^{2}\right)$ Cf., F. Braun, Wied. Ann. 16 (1852), pp. 562.
when $A$ means the electrochemical equivalent of the metal, $P$ means the stress in kilograms of weight per square millimeter, $v$ is the elongation in centimeters under elastic aftereffect, which again compensates for the stress $P$, and $m$ means the mass of the wire.

Let $P$ be taken to be equal to the stress that will temporarily lengthen a wire that is 1 m in length by 1 mm , and likewise let $v-1 \mathrm{~mm}$. One will then have:

|  | Copper |  |  | Silver |  |
| :---: | :---: | :--- | ---: | :--- | :--- |
| $P=$ | 12 | kilogram weight | $P=$ | 7.4 | kilogram weight |
| $v=$ | 0.1 | cm | $v=$ | 0.1 | cm |
| $A$ | $=64$ | g | $A=216$ | g |  |
| $m=$ | 8.9 | g | $m=$ | 10.3 | g |
| $e$ | $=4.5$ | microvolt | $e=$ | 7.9 | microvolt |

Those forces, in and of themselves, would be observed if the other known complications did not exist. Meanwhile, if the deformations are taken to be small then the phenomenon would probably prove to be easiest to verify for torsion, for which the energy per unit volume is greater in the outer surface lays than it is inside of the wire.
5. - One must assume that changes in the internal work capacity are exceptionally greater in very thinly deposited layers of metals or electrolytes if one would like to use that to explain the electromotive forces in thin metallic coatings that Oberbeck $\left({ }^{1}\right)$ recently measured or the slow growth of the force in a chain $\mathrm{Pb}\left|\mathrm{Pb} \mathrm{Br}_{2}\right| \mathrm{Br} \mid \mathrm{Pt}$ that I had occasionally observed in the past $\left(^{2}\right)$. In both cases, the thicker layer behaved like the negative pole of the chain, so the free energy of the unit weight must be greater in it that it is in the thin layer. Whether changes in the mechanical work capacity of such enormous magnitudes as would be required to explain those observations are conceivable seems questionable to me, and I believe that one must revert to the analogy with catalytic phenomena that I emphasized before.
6. - I shall briefly return once more to the elastic aftereffects. One imagines that a wire is continuously enveloped adiabatically. If one stretches it and keeps at constant tension for a long time such that it assumes elastic aftereffects and then lets the tension again drop back to the initial tension and finally once more vanish under that elastic aftereffect then the point $(p, v)$ that represented the state of the body will have almost traversed a closed curve. It is not completely closed for the following reason: As a graphical representation will show, the system has consumed work (which is supplied from the outside), so as a result, the final temperature must be higher than the initial temperature. Even when the deformation due to the elastic aftereffect already occurs during the alternation of the tensions, the same thing will be true. That is the explanation for the phenomenon that Villari ${ }^{3}{ }^{3}$ ) observed, in which rubber exhibited a rise in temperature after rapid
$\left.{ }^{1}{ }^{1}\right)$ Oberbeck, Wied. Ann. 31 (1887), pp. 337.
( ${ }^{2}$ ) Braun, Wied. Ann. 17 (1882), pp. 602.
$\left(^{3}\right)$ Villari, Pogg. Ann. 144 (1872), pp. 274.
stretching and relaxation. Permanent deformations were also be produced in his experiments. However, that is not the main basis for the phenomenon, which emerges from the fact that a rapid repetition of stretching and relaxation in which the same initial state (except for the change in temperature) is soon reached again and again will increase the temperature. Metals, which exhibit a different thermal effect under stretching, must also behave like rubber, i.e., they must heat up.
7. - In the foregoing, the assumption was always made that the changes happened continuously, and continuity was defined in the known way such that an infinitely-small change in one of the variables would also be coupled with just infinitely-small changes in all of the others. One then asks: Within what limits can one speak of a system of continuous changes, i.e., inside of what limits are the theorems above applicable? That question appears very often, and in particular in the mechanical theory of heat, it often takes the form of saying, e.g., a very-small change in temperature (which we already consider to be harmlessly identifiable with an infinitesimal that appears in the formulas, because it lies at the limits of measurability) is coupled with a change in one of the other variables, e.g., the pressure, which we do not regard as one of the infinitely-small, sufficiently-close ones in other cases.

As far as calculation is concerned, one merely needs to do the following: Let $f(x, y)=z$ be a function of the variables $x, y$. The necessary and sufficient condition for the change $d x$ to be regarded as infinitely small is that:

$$
\frac{\partial f(x, y)}{\partial y}=\frac{\partial f(x+d x, y)}{\partial y} \quad \text { and } \quad \frac{\partial f(x, y)}{\partial x}=\frac{\partial f(x+d x, y)}{\partial x} .
$$

However, that is always the case within the region for which the total change in the function can be represented as a linear function of the changes in the variables to the degree of precision that is desired. How far that region extends then depends upon:

1) the special case,
2) the desired degree of precision.

For example, for the relationship between adiabatic changes in temperature and pressure in water at $0^{\circ}$ and a desired precision of $1 \%$, when the region can be bounded by a rectangle, the following will be true:

Let $z=v$ (volume), $x=t, y=p$.
a) From the numbers that $\mathbf{F}$. Kohlrausch compiled from the measurements of different observes, the change in density was equal to:

$$
\begin{array}{ll}
0.00005 & \text { from } 0^{\circ} \text { to } 1^{\circ}, \\
0.00004 & \text { from } 1^{\circ} \text { to } 2^{\circ} .
\end{array}
$$

If one calculates a second-degree interpolating equation from that then it will follow that the region goes from 0 to $0.11^{\circ} \mathrm{C}$ along the $t$-axis.
b) On the other hand, $\partial v / \partial p=-m v$. If one sets $m$ equal to a constant then that will give a change in volume for 10 atmospheres that deviates by less than $0.04 \%$ from the one that one calculates when one introduces $m$ as something that depends upon pressure [under the assumption of a linear dependency on the Cailletet observations $\left(^{1}\right)$ ]. The fact that $v$ depends upon $p$ does not come under consideration in the conditions that are imposed. In that way of thinking, a change of ten atmospheres would still be regarded as infinitely small.
c) One then asks how $\partial^{2} v / \partial t \partial p$ behaves and whether a restriction of the region might perhaps enter in because of its value. According to Grassi, the compressibility of water decreases by around $2 \%$ when one goes from $0^{\circ}$ to $1.5^{\circ}$, so by $1 \%$ for $0.7^{\circ}$. No further narrowing of the region in the direction of the temperature axis will enter in that way.

The result would be that a temperature increase of only $0.11^{\circ} \mathrm{C}$ could then be considered to be an infinitely-small change to a desired precision of $1 \%$, as opposed to a pressure increase of at least ten atmospheres. [Condition b) alone would allow, say, 200 atmospheres.]

The region changes from case to case. For example, for mercury, it would be much larger in the direction of the temperature axis, so one could perhaps consider changes of several degrees to be infinitely small in that case.
${ }^{(1)}$ Cf., Wüllner, Lehrbuch, $4^{\text {th }}$ ed., v. 1, pp. 274, et seq.


[^0]:    $\left({ }^{1}\right)$ I recently published the theorem that is communicated in what follows without proof in Zeitschrift für physikalische Chemie (1, pp. 269) and applied it to a few cases.

[^1]:    $\left.{ }^{( }{ }^{1}\right)$ F. Braun, Wied. Ann. 30 (1887), pp. 250. Cf., also the decomposition under pressure that was described by Spring and van't Hoff, which can also be regarded as a solubility phenomenon. Zeit. phys. Chem. 1 (1887), pp. 227.
    $\left({ }^{2}\right)$ The thermo-diffusion that Sorret discovered must also be included in this theorem. In an everywhere-equally concentrated solution, a diffusion current must arise whenever the temperature is no longer constant. If an immigration of salt particles brings about a lowering of temperature (and an emigration produces a temperature increase) then the warmer location will be richer in salt; that is the case that Sorret observed. A reverse diffusion current must occur when the effect of the heat changes its sign.
    $\left.{ }^{(3}\right)$ Von Helmholtz, Ges. Abhandlungen, v. 2, pp. 962.

[^2]:    ( ${ }^{1}$ ) Riecke, Gött. Nachr. no. 7, 1887.
    $\left(^{2}\right)$ A saturated element of $\mathrm{Zn} \mid \mathrm{ZnSO}_{4}$ (sat. $\mid \mathrm{ZnSO}_{4}+8$ vol. $\mathrm{H}_{2} \mathrm{O} \mid \mathrm{Zn}$ ) exhibits a regular increase in electromotive force when the pressure is raised by a few hundred atmospheres. It can easily be brought to 1.45 times its value at atmospheric pressure. A current that goes in the direction of the chain current must then bring about a decrease in volume, which is also the case. A quantitative consequence of that fact would also allow one to decide whether and how the electrolytic transport changes with pressure. From F. Kohlrausch's theory of the resistance of solutions, the changes in those quantities with pressure that J. Fink verified might then become explainable. [Wied. Ann. 26 (1885), pp. 481].

[^3]:    $\left.{ }^{( }{ }^{1}\right)$ Cf., Graetz, Wied. Ann. 28 (1886), pp. 354.
    $\left(^{2}\right)$ Joule, Phil. Trans. 149 (1859), pp. 119. Cf., also loc. cit., pp. 100.
    ${ }^{3}$ ) Joule, loc. cit., pp. 101.
    $\left({ }^{4}\right)$ Joule, loc. cit., pp. 118.

