Theorem of the equivalence of transformations.

Carnot's theorem, when brought into agreement with the first fundamental theorem, expresses a relation between two kinds of transformations, the transformation of heat into work, and the passage of heat from a warmer to a colder body, which may be regarded as the transformation of heat at a higher, into heat at a lower temperature. The theorem, as hitherto used, may be enunciated in some such manner as the following:—In all cases where a quantity of heat is converted into work, and where the body effecting this transformation ultimately returns to its original condition, another quantity of heat must necessarily be transferred from a warmer to a colder body; and the magnitude of the last quantity of heat, in relation to the first, depends only upon the temperatures of the bodies between which heat passes, and not upon the nature of the body effecting the transformation.

In deducing this theorem, however, a process is contem-



plated which is of too simple a character; for only two bodies losing or receiving heat are employed, and it is tacitly assumed that one of the two bodies between which the transmission of heat takes place is the source of the heat which is converted into work. Now by previously assuming, in this manner, a particular temperature for the heat converted into work, the influence which a change of this temperature has upon the relation between the two quantities of heat remains concealed, and therefore the theorem in the above form is incomplete.

It is true this influence may be determined without great difficulty by combining the theorem in the above limited form with the first fundamental theorem, and thus completing the former by the introduction of the results thus arrived at. But by this indirect method the whole subject would lose much of its clearness and facility of supervision, and on this account it appears to me preferable to deduce the general form of the theorem immediately from the same principle which I have already employed in my former memoir, in order to demonstrate the modified theorem of Carnot.

This principle, upon which the whole of the following development rests, is as follows:—Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time*. Everything we know concerning

* [The principle may be more briefly expressed thus: Heat cannot by itself pass from a colder to a warmer body; the words "by itself," (von selbst) however, here require explanation. Their meaning will, it is true, be rendered sufficiently clear by the expositions contained in the present memoir, nevertheless it appears desirable to add a few words here in order to leave no doubt as to the signification and comprehensiveness of the principle.

In the first place, the principle implies that in the immediate interchange of heat between two bodies by conduction and radiation, the warmer body never receives more heat from the colder one than it imparts to it. The principle holds, however, not only for processes of this kind, but for all others by which a transmission of heat can be brought about between two bodies of different temperatures, amongst which processes must be particularly noticed those wherein the interchange of heat is produced by means of one or more bodies which, on changing their condition, either receive heat from a body, or impart heat to other bodies.

On considering the results of such processes more closely, we find that in one and the same process heat may be carried from a colder to a warmer body and another quantity of heat transferred from a warmer to a colder body without any other permanent change occurring. In this case we have not a





the interchange of heat between two bodies of different temperatures confirms this; for heat everywhere manifests a tendency to equalize existing differences of temperature, and therefore to pass in a contrary direction, *i. e.* from warmer to colder bodies. Without further explanation, therefore, the truth of the principle will be granted.

For the present we will again use the well-known process first conceived by Carnot and graphically represented by Clapeyron, with this difference, however, that, besides the two bodies between which the transmission of heat takes place, we shall assume a third, at any temperature, which shall furnish the heat converted into work. An example being the only thing now required, we shall choose as the changing body one whose changes are governed by the simplest possible laws, e.g. a permanent gas*. Let, therefore, a quantity of permanent gas having the temperature t and volume v be given. In the adjoining figure we shall suppose the volume represented by the abscissa o h, and the pressure exerted by the gas at this volume, and at the tem-

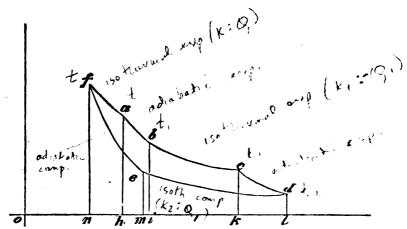
simple transmission of heat from a colder to a warmer body, or an tescending transmission of heat, as it may be called, but two connected transmissions of opposite characters, one ascending and the other descending, which compensate each other. It may, moreover, happen that instead of a descending transmission of heat accompanying, in the one and the same process, the ascending transmission, another permanent change may occur which has the peculiarity of not being reversible without either becoming replaced by a new permanent change of a similar kind, or producing a descending transmission of heat. In this case the ascending transmission of heat may be said to be accompanied, not immediately, but mediately, by a descending one, and the permanent change which replaces the latter may be regarded as a compensation for the ascending transmission.

Now it is to these compensations that our principle refers; and with the aid of this conception the principle may be also expressed thus: an uncompensated transmission of heat from a colder to a warmer body can never occur. The term "uncompensated" here expresses the same idea as that which was intended to be conveyed by the words "by itself" in the previous enunciation of the principle, and by the expression "without some other change, connected therewith, occurring at the same time" in the original text.—1864.]

* [It will readily be understood that everything here said, by way of example, concerning a gas applies, essentially, to every other body whose condition is determined by its temperature and volume. Of course the shapes of the curves, representing the decrease of pressure corresponding to an augmentation of volume, differ for different bodies; in other words, the aspect of the figure will depend upon the choice of the body.—1864.]

perature t, by the ordinate ha. This gas we subject, successively, to the following operations:—

1. The temperature t of the gas is changed to t_1 , which, for Fig. 7.



the sake of an example, may be less than t. To do this, the gas may be enclosed within a surface impenetrable to heat, and allowed to expand without either receiving or losing heat. The diminution of pressure, consequent upon the simultaneous increase of volume and decrease of temperature, is represented by the curve ab; so that, when the temperature of the gas has reached t_1 , its volume and pressure have become oi and ib respectively.

- 2. The gas is next placed in communication with a body K_1 , of the temperature t_1 , and allowed to expand still more, in such a manner, however, that all the heat lost by expansion is again supplied by the body. With respect to this body, we shall assume that, owing to its magnitude or to some other cause, its temperature does not become appreciably lower by this expenditure of heat, and therefore that it may be considered constant. Consequently, during expansion the gas will also preserve a constant temperature, and the diminution of the pressure will be represented by a portion of an equilateral hyperbola b c. The quantity of heat furnished by K_1 shall be Q_1 .
- 3. The gas is now separated from the body K_1 and allowed to expand still further, but without receiving or losing heat, until its temperature has diminished from t_1 to t_2 . The consequent diminution of pressure is represented by the curve $c \, d$, which is of the same nature as $a \, b$.
 - 4. The gas is now put in communication with a body K2,

having the constant temperature t_2 , and compressed; all the heat thus produced in it being imparted to K_2 . This compression is continued until K_2 has received the same quantity of heat Q_1 as was before furnished by K_1 . The pressure will increase according to the equilateral hyperbola de.

- 5. The gas is then separated from the body K_2 and compressed, without being permitted to receive or lose heat, until its temperature rises from t_2 to its original value t, the pressure increasing according to the curve ef. The volume of n to which the gas is thus reduced is smaller than its original volume of h, for the pressure which had to be overcome in the compression df e, and therefore the work to be spent, were less than the corresponding magnitudes during the expansion df c; so that, in order to restore the same quantity of heat G, the compression must be continued further than would have been necessary merely to annul the expansions.
- 6. The gas is at length placed in communication with a body K, of the constant temperature t, and allowed to expand to its original volume oh, the body K replacing the heat thus lost, the amount of which may be Q. When the gas reaches the volume oh with the temperature t, it must exert its original pressure; and the equilateral hyperbola, which represents the last diminution of pressure, will precisely meet the point a.

These six changes together constitute a cyclical process, the gas ultimately returning to its original condition. Of the three bodies K, K_1 and K_2 , which throughout the whole process are considered merely as sources or reservoirs of heat, the two first have lost the quantities of heat Q and Q_1 , and the third has received the quantity Q_1 , or, as we may express it, Q_1 has been transferred from K_1 to K_2 , and Q has disappeared. The last quantity of heat must, according to the first theorem, have been converted into exterior work. The pressure of the gas during expansion being greater than during compression, and therefore the positive amount of work greater than the negative, there has been a gain of exterior work, which is evidently represented by the area of the closed figure $a \ b \ c \ d \ e \ f$. If we call this amount of work W, then, according to equation (1),

$$Q=A.W*$$

^{* [}The cyclical process here described differs from the one described at

The whole of the above-described cyclical process may be reversed or executed in an opposite manner by connecting the gas with the same bodies and, under the same circumstances as before, executing the reverse operations, i. e. commencing with the compression af, after which would follow the expansions fe and ed, and lastly the compressions dc, cb, and ba. The bodies K and K_1 will now evidently receive the quantities of heat Q and Q_1 , and K_2 will lose the quantity Q_1 . At the same time the negative work is now greater than the positive, so that the area of the closed figure now represents a loss of work. The result of the reverse process, therefore, is that the quantity of heat Q_1 has been transferred from K_2 to K_1 , and the quantity of heat Q, generated from work, given to the body K.

In order to learn the mutual dependence of the two simultaneous transformations above described, we shall first assume that the temperatures of the three reservoirs of heat remain the same, but that the cyclical processes through which the transformations are effected are different. This will be the case when, instead of a gas, some other body is submitted to similar transformations, or when the cyclical processes are of any other kind, subject only to the conditions that the three bodies K, K, and K₂ are the only ones which receive or impart heat, and of the two latter the one receives as much as the other loses. several processes can be either reversible, as in the foregoing case, or not, and the law which governs the transformations will vary accordingly. Nevertheless the modification which the law for non-reversible processes suffers may be easily applied afterwards, so that at present we will confine ourselves to the consideration of reversible cyclical processes.

page 23 of the First Memoir, and there graphically represented in fig. 1, only by the circumstance that three, instead of two bodies, serving as reservoirs of heat, now present themselves. If we assume the temperature t of the body K to be equal to the temperature t_1 of the body K_1 , we may dispense with the body K altogether, and instead thereof employ the body K_1 ; the result of this would be that the body K_1 would give up, on the whole, the quantity $Q+Q_1$ of heat, and the body K_2 would receive the quantity Q_1 . It would then be said that of the total quantity of heat given up by the body K_1 , the portion Q is transformed into work, and the other part Q_1 is transferred to the body K_2 ; but this occurred in the previously described process, so that the latter must be regarded as a special case of the one here described.—1864.

With respect to all these it may be proved from the foregoing principle, that the quantity of heat Q1, transferred from K1 to K₂, has always the same relation to Q, the quantity of heat transformed into work. For if there were two such processes wherein, Q being the same, Q, was different, then the two processes could be executed successively, the one in which Q1 was smaller in a direct, the other in an opposite manner. quantity of heat Q, which by the first process was converted into work, would be again transformed into heat by the second process and restored to the body K, and in other respects everything would ultimately return to its original condition; with this sole exception, however, that more heat would have passed from Ke to K, than in the opposite direction. On the whole, therefore, a transmission of heat from a colder body K₂ to a warmer K, has occurred, which in contradiction to the principle before mentioned, has not been compensated in any manner.

Of the two transformations in such a reversible process either can replace the other, if the latter is taken in an opposite direction; so that if a transformation of the one kind has occurred, this can be again reversed, and a transformation of the other kind may be substituted without any other permanent change being requisite thereto. For example, let the quantity of heat Q, produced in any manner whatever from work, be received by the body K; then by the foregoing cyclical process it can be again withdrawn from K and transformed back into work, but at the same time the quantity of heat Q₁ will pass from K₁ to K₂; or if the quantity of heat Q₁ had previously been transferred from K₁ to K₂, this can be again restored to K₁ by the reversed cyclical process whereby the transformation of work into the quantity of heat Q of the temperature of the body K will take place.

We see, therefore, that these two transformations may be regarded as phenomena of the same nature, and we may call two transformations which can thus mutually replace one another equivalent. We have now to find the law according to which the transformations must be expressed as mathematical magnitudes, in order that the equivalence of two transformations may be evident from the equality of their values. The mathematical value of a transformation thus determined may be called its equivalence-value (Aequivalenzwerth).

With respect to the direction in which each transformation is to be considered positive, it may be chosen arbitrarily in the one, but it will then be fixed in the other, for it is clear that the transformation which is equivalent to a positive transformation must itself be positive. In future we shall consider the conversion of work into heat and, therefore, the passage of heat from a higher to a lower temperature as positive transformations*.

With respect to the magnitude of the equivalence-value, it is first of all clear that the value of a transformation from work into heat must be proportional to the quantity of heat produced; and besides this it can only depend upon the temperature. Hence the equivalence-value of the transformation of work into the quantity of heat Q, of the temperature t, may be represented generally by

$$\mathbf{Q} \cdot f(t)$$
,

wherein f(t) is a function of the temperature, which is the same for all cases. When Q is negative in this formula, it will indicate that the quantity of heat Q is transformed, not from work into heat, but from heat into work. In a similar manner the value of the passage of the quantity of heat Q, from the temperature t_1 to the temperature t_2 , must be proportional to the quantity Q, and besides this, can only depend upon the two temperatures. In general, therefore, it may be expressed by

$$\mathbf{Q} \cdot \mathbf{F}(t_1, t_2)$$
,

wherein $F(t_1, t_2)$ is a function of both temperatures, which is the same for all cases, and of which we at present only know that, without changing its numerical value, it must change its sign when the two temperatures are interchanged; so that

$$F(t_2, t_1) = -F(t_1, t_2).$$
 (4)

In order to institute a relation between these two expressions, we have the condition, that in every reversible cyclical process of the above kind, the two transformations which are involved must be equal in magnitude, but opposite in sign; so that their algebraical sum must be zero. For instance, in the process for



^{* [}The reason why this choice of the positive and negative senses is preferable to the opposite one, will become apparent after the theorems relative to the transformations have been enunciated.—1864.]

a gas, so fully described above, the quantity of heat Q, at the temperature t, was converted into work; this gives $-Q \cdot f(t)$ as its equivalence-value, and that of the quantity of heat Q_1 , transferred from the temperature t_1 to t_2 , will be $Q_1 \cdot F(t_1, t_2)$, so that we have the equation

$$-Q \cdot f(t) + Q_1 \cdot F(t_1, t_2) = 0.$$
 (5)

Let us now conceive a similar process executed in an opposite manner, so that the bodies K_1 and K_2 , and the quantity of heat Q_1 passing between them, remain the same as before; but that instead of the body K of the temperature t, another body K' of the temperature t' be employed; and let us call the quantity of heat produced by work in this case Q',—then, analogous to the last, we shall have the equation

$$Q'.f(t') + Q_1.F(t_2, t_1) = 0.$$
 (6)

Adding these two equations, and applying (4), we have

$$-Q \cdot f(t) + Q' \cdot f(t') = 0.$$
 (7)

If now we regard these two cyclical processes together as one cyclical process, which is of course allowable, then in the latter the transmissions of heat between K₁ and K₂ will no longer enter into consideration, for they precisely cancel one another, and there remain only the quantity of heat Q taken from K and transformed into work, and the quantity Q' generated by work and given to K'. These two transformations of the same kind, however, may be so divided and combined as again to appear as transformations of different kinds. If we hold simply to the fact that a body K has lost the quantity of heat Q, and another body K' has received the quantity Q', we may without hesitation consider the part common to both quantities as transferred from K to K', and regard only the other part, the excess of one quantity over the other, as a transformation from work into heat, or vice versd. For example, let the temperature t' be greater than t, so that the above transmission, being a transmission from the colder to the warmer body, will be negative. Then the other transformation must be positive, that is, a transformation from work into heat, whence it follows that the quantity of heat Q' imparted to K' must be greater than the quantity Q lost by K. If we divide Q' into the two parts

$$Q$$
 and $Q'-Q$,

the first will be the quantity of heat transferred from K to K', and the second the quantity generated from work.

According to this view the double process appears as a process of the same kind as the two simple ones of which it consists; for the circumstance that the generated heat is not imparted to a third body, but to one of the two between which the transmission of heat takes place, makes no essential difference, because the temperature of the generated heat is arbitrary, and may therefore have the same value as the temperature of one of the two bodies; in which case a third body would be superfluous. Consequently, for the two quantities of heat Q and Q'—Q, an equation of the same form as (6) must hold, i. e.

$$(Q'-Q).f(t')+Q.F(t,t')=0.$$

Eliminating the magnitude Q' by means of (7), and dividing by Q, this equation becomes

so that the temperatures t and t' being arbitrary, the function of two temperatures which applies to the second kind of transformation is reduced, in a general manner, to the function of one temperature which applies to the first kind.

For brevity, we will introduce a simpler symbol for the last function, or rather for its reciprocal, inasmuch as the latter will afterwards be shown to be the more convenient of the two. Let us therefore make

so that T is now the unknown function of the temperature involved in the equivalence-values. Further, T_1 , T_2 , &c. shall represent particular values of this function, corresponding to the temperatures t_1 , t_2 , &c.

According to this, the second fundamental theorem in the mechanical theory of heat, which in this form might appropriately be called the theorem of the equivalence of transformations, may be thus enunciated:

If two transformations which, without necessitating any other permanent change, can mutually replace one another, be called



equivalent, then the generation of the quantity of heat Q of the temperature t from work, has the equivalence-value

Q 不

and the passage of the quantity of heat Q from the temperature t_1 to the temperature t_2 , has the equivalence-value

$$Q\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

wherein T is a function of the temperature, independent of the nature of the process by which the transformation is effected.

If to the last expression we give the form

$$\frac{Q}{T_2} - \frac{Q}{T_1}$$

it is evident that the passage of the quantity of heat Q, from the temperature t_1 to the temperature t_2 , has the same equivalence-value as a double transformation of the first kind, that is to say, the transformation of the quantity Q from heat at the temperature t_1 into work, and from work into heat at the temperature t_2 . A discussion of the question how far this external agreement is based upon the nature of the process itself would be out of place here*; but at all events, in the mathematical determination of the equivalence-value, every transmission of heat, no matter how effected, can be considered as such a combination of two opposite transformations of the first kind.

By means of this rule, it will be easy to find a mathematical expression for the total value of all the transformations of both kinds, which are included in any cyclical process, however complicated. For instead of examining what part of a given quantity of heat received by a reservoir of heat, during the cyclical process, has arisen from work, and whence the other part has come, every such quantity received may be brought into calculation as if it had been generated by work, and every quantity lost by a reservoir of heat, as if it had been converted into work. Let us assume that the several bodies K_1 , K_2 , K_3 , &c., serving as reservoirs of heat at the temperatures t_1 , t_2 , t_3 , &c., have received during the process the quantities of heat Q_1 , Q_2 , Q_3 , &c., whereby the loss of a quantity of heat will be counted

[* This subject is discussed in one of the subsequent memoirs.—1864.]

as the gain of a negative quantity of heat; then the total value N of all the transformations will be

$$N = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \&c. . = \Sigma \frac{Q}{T}. (10)$$

It is here assumed that the temperatures of the bodies K_1 , K_2 , K_3 , &c. are constant, or at least so nearly constant, that their variations may be neglected. When one of the bodies, however, either by the reception of the quantity of heat Q itself, or through some other cause, changes its temperature during the process so considerably that the variation demands consideration, then for each element of heat dQ we must employ that temperature which the body possessed at the time it received it, whereby an integration will be necessary. For the sake of generality, let us assume that this is the case with all the bodies; then the foregoing equation will assume the form

$$\mathbf{N} = \int \frac{d\mathbf{Q}}{\mathbf{T}}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

wherein the integral extends over all the quantities of heat received by the several bodies.

If the process is reversible, then, however complicated it may be, we can prove, as in the simple process before considered, that the transformations which occur must exactly cancel each other, so that their algebraical sum is zero.

For were this not the case, then we might conceive all the transformations divided into two parts, of which the first gives the algebraical sum zero, and the second consists entirely of transformations having the same sign. By means of a finite or infinite number of simple cyclical processes, the transformations of the first part must admit of being cancelled*, so that the transformations of the second part would alone remain

* [By a simple cyclical process is here to be understood one in which, as above described, a quantity of heat is transformed into, or arises from work, whilst a second quantity is transferred from one body to another. Now it may be readily shown that every two transformations whose algebraical sum is zero may be cancelled by means of one or two simple cyclical processes.

In the first place, let the two given transformations be of different kinds. For instance, let the quantity of heat Q at the temperature t be transformed nto work, and the quantity Q_1 be transferred from a body K_1 of the tempera-



without any other change. Were these transformations negative, i. e. transformations from heat into work, and passages of heat from lower to higher temperatures, then of the two kinds the first could be replaced by transformations of the

ture t_1 to a body K_2 of the temperature t_2 , whereby we will assume, since our intended exposition will be thereby facilitated, that Q and Q_1 denote the absolute values of the quantities of heat, so that the positive or negative character of each transformation must be denoted explicitly by a prefixed + or - sign. Suppose, moreover, that the magnitudes of the two quantities of heat are related to one another in the manner expressed by the equation

$$-\frac{Q}{T}+Q_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=0.$$

Conceive the cyclical process above described to be performed in a contrary manner, so that the quantity of heat Q at the temperature t arises from work, and another quantity of heat is transferred from the body K_2 to the body K_1 . This latter quantity must then be precisely the quantity Q_1 , which enters into the above equation, and thus the given transformations are cancelled.

In the next place, let a transformation from work to heat, and another from heat to work be given; for instance, let the quantity of heat Q, at the temperature t, be generated by work, and the quantity Q', at the temperature t', be converted into work, and suppose the two quantities to be so related to one another that

$$\frac{\mathbf{Q}}{\mathbf{T}} - \frac{\mathbf{Q'}}{\mathbf{T'}} = 0.$$

Conceive the above-described cyclical process to be first performed, whereby the quantity of heat Q at the temperature t is converted into work, and another quantity Q_1 transferred from a body K_1 to another body K_2 . Afterwards conceive a second cyclical process of the opposite kind to be performed, in which the last-named quantity of heat Q_1 is transported back from K_2 to K_1 , and, besides this, a quantity of heat of the temperature t' is generated from work. This conversion of work into heat must then, apart from its sign, be equivalent to the preceding conversion of heat into work, since both are equivalent to one and the same transmission of heat. The heat at the temperature t', which has arisen from work, must consequently be just as great as the quantity Q' involved in the last equation, and the given transformations are thus cancelled.

In the last place, let two transmissions of heat be given; for instance, let the quantity of heat Q_1 be transferred from a body K_1 , of the temperature t_1 , to a body K_2 of the temperature t_2 , and let another quantity Q_1 be conveyed from a body K_2 , of the temperature t_2 , to a body K_1 , of the temperature t_1 , and suppose these two quantities to stand to each other in the relation

Conceive now two cyclical processes to be performed, in one of which the quantity of heat Q_1 is carried from K_2 to K_1 , and thereby the quantity Q at the temperature t generated by work, whilst in the second the same quan-

latter kind*, and ultimately transmissions of heat from a lower to a higher temperature would alone remain, which would be compensated by nothing, and therefore contrary to the above principle. Further, were those transformations *positive*, it would only be necessary to reverse the operations in order to render them negative, and thus we should again obtain the foregoing impossible case. Hence we conclude that the second part of the transformations can have no existence.

Consequently the equation

$$\int \frac{dQ}{T} = 0 \quad . \quad . \quad . \quad . \quad . \quad (II)$$

is the analytical expression, for all reversible cyclical processes, of the second fundamental theorem in the mechanical theory of heat.

The application of this equation can be considerably extended by giving to the magnitude t involved in it a somewhat different signification. For this purpose, let us consider a cyclical process consisting of a series of changes of condition made by a

tity of heat Q is reconverted into work, and thereby another quantity transferred from K'_1 to K'_2 . This other quantity must then be precisely that which is denoted by Q_1' , and the two given transformations are thus cancelled.

If now, instead of two, any number of transformations were given, having an algebraical sum equal to zero, we could always separate and combine them so as to obtain, solely, groups consisting each of two transformations whose algebraical sum is equal to zero; and the two transformations of each such group could then, as has just been shown, be cancelled by means of one or two simple cyclical processes. If continuous changes of temperature should present themselves in the given original process, so that the quantities of heat given up and received would have to be divided into infinitesimal elements, the number of the groups which would have to be formed, and consequently also the number of simple cyclical processes, would be infinite; as far as the principle is concerned, however, this makes no difference.—
1864.]

* [For if the given transformation consist in the conversion into work of the quantity of heat Q at the temperature t, we have, as already explained in the text in reference to the opposite case, merely to conceive the above-described cyclical process performed in a contrary manner, whereby the quantity of heat Q at the temperature t will be generated by work; and at the same time another quantity Q_1 will be transferred from a body K_2 , of the temperature t_2 , to a body K_1 of the higher temperature t_1 . The given transformation from heat to work will thus be cancelled, and replaced by the transmission of heat from K_1 to K_2 .—1864.]