A KINETIC EXPLANATION
OF ADIABATIC COMPRESSION

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In physical chemistry, and in practical calculation problems of industrial chemical operations, a phenomenological treatment, viz.: one using thermodynamics, concept of similarity, or dimensional analysis, is generally preferred. In both subjects, however, a causal explanation of phenomena, viz.: by the kinetic theory of gases, statistical mechanics, etc., seems to come into prominence. Though causal explanation throws more light on the essential character of the process, it is, in most cases, less suitable for computation or for the solving of design problems, because of the inaccurancies from the inevitable omissions and approximations involved.[1]

The formulas used in the phenomenological method are deduced from experimental data and, thus, furnish quite precise correlations for practical purposes, and do not require an explanation based on the essential character of the phenomenon in question.

In our tuition these two methods go side by side, but, unfortunately, without being made clear to the students that these methods are equally valuable and that, specially nowadays, the causal treatment is able to furnish formulas completely equivalent with those derived by phenomenological considerations.[2]

Using adiabatic compression as a simple model, endeavour will be made to show here that the result of a treatment by the kinetic theory of gases is the same exact and convenient formula arrived at by the phenomenological

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[1] In the present paper "causal treatment" figures as the opposite of phenomenological treatment which does not consider the causes of phenomena and processes. Perhaps it would be more correct to speak about the "theory that reveals the laws of physics involved in interactions", and state this theory as the opposite of a phenomenological treatment. The theory dealing with interactions covers both simple causality: a reduction to a few causes, and statistical correlations due to a comprehensive view of the more complex and numerous interactions. Nevertheless, the more simple apellation "causal correlation" has been chosen here because, as will be shown later, in the subjects mentioned, phenomena can be traced back to some simple, well-defined causal interactions. The above restriction through inaccuracy refers just to this, that in the causal deductions some interactions which are difficult to assess and are of no marked influence, are usually included as approximations or at not very exact values.

[2] Of course, when these two methods are contrasted, quantitative phenomenology is always understood, which uses mathematical methods; also the deterministic character of phenomenology has to be accepted.

—thermodynamical method. Moreover, by reducing the thermodynamical events to one single cause: to the exchange of impulses, a causal explanation of the phenomena is also given. Thus, with a better exposition of the essentials of the process, a more intimate contact with a modern view of Nature is established.

The correlations between the characteristics of state of any adiabatic process can be derived thermodynamically as follows.

The energy change of any gas is $dE = \delta A + \delta Q$, or $\delta Q = dE - \delta A$. The change of energy of an ideal gas is $dE = C_v \cdot dT$. Work, in the case of any gas, is $\delta A = -p \cdot dV$. In the case of an ideal gas, and reversibility being stipulated, $\delta A = -\dfrac{R \cdot T}{V} \cdot dV$, or, because $R = C_p - C_v$,

$$\delta A = -(C_p - C_v) \cdot \frac{T}{V} \cdot dV \cdot \text{ Therefore,}$$

$$\delta Q = C_v \cdot dT + (C_p - C_v)\, T\, \frac{dV}{V} = 0\,, \quad \frac{dT}{T} = -(\varkappa - 1)\frac{dV}{V}\,,$$

then, by integration, $ln\, T = -(\varkappa - 1)\, ln\, V + C$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\varkappa-1}$$

The deduction is wholly formal, phenomenological. From verified correlations the required physical correlations have been worked out mathematically, but nothing has been revealed about the physical occurancies taking place during the adiabatic process.

Adiabatic compression according to the kinetic theory of gases

The average velocity of the molecules at temperature T, in accordance with the kinetic theory of gases

$$\bar{c} = \sqrt{\frac{8}{\pi} \cdot \frac{RT}{M}} \tag{1}$$

For the sake of simplicity, let the gas enclosed in the cylinder be a monatomic gas, e.g. argon, then $M_A = 39.91$, $\bar{c} = 380$ (m/sec) at 273° K. Let the move-

ment of the gas be an ordered movement in three directions (Fig. 1). The molecule confined in space moves to and fro. The time between two impacts on the wall, $\tau = \dfrac{2L}{\bar{c}}$, the number of impacts on the surface of the piston of one molecule in unit time, $z = \dfrac{1}{\tau} = \dfrac{\bar{c}}{2L}$ (sec^{-1}), the sum of the number of impacts on the surface of the piston in unit time

$$Z = \Sigma\, z = \frac{N}{3} \cdot \frac{\bar{c}}{2L} \tag{2}$$

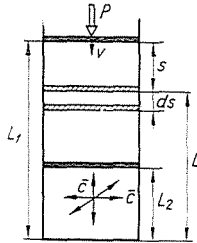In this formula N is the number of the molecules of the gas enclosed in the cylinder.

Fig. 1

The velocity of the movement of the piston is v(m/sec) and in the time interval dt the travelled distance is ds, $dt = \dfrac{ds}{v}$: query, what is the number of impacts on the piston during this time.

$$Z \cdot dt = \frac{N\bar{c}}{6L} \cdot dt \tag{3}$$

$L = L_{(t)}$ is a function of time t. If the piston moves with uniform velocity v, (and the presupposition of this uniform velocity is essential this being the criterion of reversibility), then $v = \dfrac{s}{t} \cdot \dfrac{L_1 - L}{t}$, and from this $L = L_1 - v \cdot t$,

$$Z \cdot dt = \frac{N\bar{c}}{6\,(L_1 - vt)} \cdot dt \tag{4}$$

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Let the direction of the movement of the piston be considered a positive magnitude (Fig. 2). At every molecular impact the moving piston transmits a certain impulse to the molecule impinging. According to the law of the impact of elastic spheres — and the molecules can be regarded as perfectly elastic spheres — the resultant velocity of rebound from the piston, $\bar{c}_r = \bar{c} + 2\,(\bar{c}^* - \bar{c})$, where $\bar{c}$ is the velocity of the molecule before impact (here: $-\bar{c}$); and $\bar{c}^*$ is the common velocity of elastic sphere and piston during impact elongation, $(m_d + m) \cdot \bar{c}^* = m_d \cdot v - m\bar{c}$. Since, however, the mass m_d of the piston is infinitely great in relation to the mass m of the molecule, $\bar{c}^* = v$, therefore,
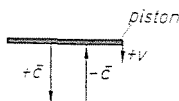

Fig. 2

$c_r = -\bar{c} + 2\,(v + \bar{c})$, $\bar{c}_r = \bar{c} + 2v$. Thus, the molecule of mass m in recoil receives and additional $\Delta i = 2m \cdot v$ impulse in relation to the stationary piston.

The total gain of impulse caused by the movement of the piston during time dt

$$\Delta i = Z.\,dt.\,2.\,m.\,v = \frac{2\,N.\,m.\,v.\,\bar{c}}{6.\,L} \cdot dt = \frac{N.\,m.\,v.\,\bar{c}}{3\,(L_1 - vt)} \cdot dt \qquad (5)$$

Note : In the case of monatomic molecules this quantity of impulse transferred through the movements of the piston is converted in its entirety into an increase of the translatory motion of the molecules, that means temperature increases. (This was why a monatomic model was chosen.) In other words, during the forward movement of the piston the number of *impacts*, i.e. the pressure, increases in the same measure. Consequently, during the time dt, the change of impulse of the translatory motion of the molecules equals the entire impulse transferred by the movement of the piston to the molecules.

In the case of monatomic molecules

$$N.\,m.\,d.\,\bar{c} = \frac{N.\,m.\,\bar{c}.\,v}{3\,(L_1 - vt)} \cdot dt \qquad (6)$$

$$\frac{1}{3} \int_0^{t_2} \frac{dt}{\frac{L_1 - t}{v}} = \int_{\bar{c}_1}^{\bar{c}_2} \frac{d\bar{c}}{\bar{c}}, \qquad -\frac{1}{3} \cdot ln\left(\frac{L_1}{v} - t\right)\Big]_{t_1 = 0}^{t_2} = ln\,\frac{\bar{c}_2}{\bar{c}_1}$$

$$\frac{1}{3} \cdot ln\,\frac{L_1}{L_1 - vt_2} = ln\,\frac{\bar{c}_2}{\bar{c}_1}, \qquad \frac{1}{3}\,ln\,\frac{L_1}{L_2} = ln\,\frac{\bar{c}_2}{\bar{c}_1},$$

therefore

$$\frac{\bar{c}_2}{\bar{c}_1} = \left(\frac{L_1}{L_2}\right)^{\frac{1}{3}} \tag{7}$$

In Equation (7) the ratio of the positions of the piston can be substituted by the ratio of the initial and final volumina:

$$\frac{\bar{c}_2}{\bar{c}_1} = \left(\frac{L_1}{L_2}\right)^{\frac{1}{3}} = \left(\frac{V_1}{V_2}\right)^{\frac{1}{3}} \tag{7a}$$

According to the kinetic theory of gases, because $\bar{c} = \sqrt{\dfrac{8}{\pi}\dfrac{RT}{M}}$,

$$\left(\frac{\bar{c}_2}{\bar{c}_1}\right)^2 = \frac{T_2}{T_1} \tag{8}$$

Based upon Equations (7a) and (8), we have

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{2}{3}} \tag{9}$$

that is, *the deduction from the kinetic theory of gases furnishes exactly the same result as that from formal thermodynamics*, and the scientific value of the kinetic explanation is enhanced by its pointing to the atomistic cause of the increase in temperature, thus showing the essence of the phenomenon.

The deduction presented is valid in the case of monatomic gases only, where the impulse generated by the piston is transformed in its entirety into translational energy.

These considerations can be applied to *polyatomic molecules* too. The translational and rotational energies of the colliding molecules are in constant interchange. At room temperature no vibration is generated yet, at higher temperatures this also enters the picture.

In the case of polyatomic molecules the impulse from the moving piston does not increase the translational energy alone, but adds to rotational, or to vibrational energies in a measure that corresponds to the excitation levels of these internal energies. This means that *a part* of the impulse originating with the moving piston is lost for the translational energy increase, and in proportion to this loss there is a *diminished increase* in the frequency of collisions, the *increase* of temperature and pressure is correspondingly *less*.

At room temperature polyatomic linear molecules possess, in addition to the three translational degrees of freedom, two rotational degrees of freedom, and polyatomic *non*-linear molecules possess three additional degrees of

freedom. Thus, the entire molecular heat, in case of complete excitation of rotations, is

$$C_s = \frac{3}{2} R + R, \quad \text{respectively,} \quad C_s = \frac{3}{2} R + \frac{3}{2} R,$$

and this means that with polyatomic linear molecules the ratio of translational energy, E_{tr}, to the total energy E_s

$$\frac{E_{tr}}{E_s} = \frac{C_{tr}}{C_s} = \frac{\frac{3}{2} R}{\frac{3}{2} R + R} = \frac{3}{5} \tag{10}$$

with polyatomic non-linear molecules

$$\frac{E_{tr}}{E_s} = \frac{C_{tr}}{C_s} \frac{\frac{3}{2} R}{\frac{3}{2} R + \frac{3}{2} R} = \frac{1}{2} \tag{11}$$

From this it follows that only three fifths or one half of the increase of impulse coming from the moving piston is used for the increase of the translational (thermal) movement of the molecules, therefore, the deduction can be carried out for polyatomic molecules as well, if the impulse increment as expressed by Equation (6) is taken, respectively, at three fifths or one half of its original value.

In this case the following values result:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{0 \cdot 4} \tag{12}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{0 \cdot 333} \tag{13}$$

It is thought that with this kinetic explanation of adiabatic compression not only a better approach towards the essence of the adiabatic process itself has been made, *i. e.* towards the perception that *adiabatic heating is caused by the macro-mechanical movement of the piston*, but the mechanistic theory of heat has also been made more clear. Inter alia also the difference between the translational energy, and the internal (rotational, vibrational) energy,[1]

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[1] In thermodynamics the entire thermal energy of a gas is designated as internal (or intrinsic, or total) energy ($E_{int} = C_v$); in the kinetic theory of gases the kinetic energy of the linear motion of molecules is called the translational energy, and the expression "internal energy of molecules" is restricted to those forms (rotational, vibrational) which are independent of linear movement $\left(E_{int} = C_v - \frac{3}{2} R\right)$

of molecules is brought into better relief. Though both are included in the term thermal movement of molecules, temperature and pressure, as was to be seen, depend only on translational energy, and the part used for the increase of intermolecular energy of the energy transferred to a gas does not increase its temperature or pressure. Consequently it is always true that

$$pV = RT = \frac{2}{3} E_{tr}$$

This modest attempt at a didactical experiment intends to show that a modern point of view concerning natural phenomena can appear not only in the selection of the scientific material to be communicated, but also in the selection of the method used for its communication. Further and beyond this, whilst debates about facts of natural science are debates purely professional, the interpretation of phenomena brings the demarcation lines between different scientific attitudes clearly to the front.

The aim of the present discussion is to express an ideology by a didactical attitude. To exclude misunderstandings it must be emphasized that no attempt is being made here to set aside the thermodynamical or phenomenological method of discussion. On the contrary, it must be acknowledged that at present in most instances a valid recognition of reality cannot be achieved by the conscious mind but through the phenomenological method, especially when confronted with more complex phenomena in the domain of applied sciences. Perhaps in most cases this method furnishes the most simple description of a phenomenon. But it must also be borne in mind that a constantly progressing recognition of Nature will bring about the extension of causal interpretations, and that causal treatment will, step by step, replace the comfortable phenomenological method, thus throwing light upon the historical role which the latter fulfils.

The question may be raised, in what measure the method of exposition demonstrated here should be classed as a new one. It seems hardly reasonable to expect that during the century that followed the investigations of Clausius the kinetic theory of gases should not have been applied to one of the simplest cases, to adiabatic compression. However, surprising it may seem, well known books about physical chemistry do not draw from kinetics, and even the qualitative treatment in them of similar thermodynamic processes eschews the application of a kinetic treatment.

PARTINGTON [1] alone takes some account of it, in the sentence:

"The heating of gases by adiabatic compression is explained by assuming that the molecules rebounding from a piston moving so as to reduce the volume of the gas acquire additional kinetic energy, since they are thrown back with higher velocity. This, however, corresponds with a higher temperature."

Unfortunately, this very lucid statement is not followed up by mathematical exposition, neither, equally surprising, can this be found in the source quoted.

KRÖNIG [2], the forerunner of Clausius, deduces only the well known correlation

$$pV = \frac{N\,m\,c^2}{6}$$

out of the change in impulse coming from collisions, but he made an error in so far as for the correct change of impulse $2 \cdot mc$ he uses the value mc in his calculations.

CLAUSIUS [3], who was prompted by Krönig's paper, goes further and deals with specific heat in a very lucid manner showing it to be the manifestation of the different forms of molecular motion. He assumes that besides translatory (linear) motion the molecules undergo rotational and vibrational motion too, and even assumes that "jedes Massenatom noch mit einer Quantität eines feineren Stoffes begabt, und dieser, ohne sich von den Atom zu trennen, doch in seiner Nähe beweglich seyn könnte," which means that he had a prevision of the excitation of electrons!

He evaluates the ratio of the translational energy, K, to the total energy, H, in the form of $\dfrac{K}{H} = \dfrac{3}{2}\left(\dfrac{c_p}{c_v} - 1\right)$ (cf. Equ. 10 and 11 of this paper) Clausius does not mention the problem dealt with here. In his collected works (4) only an attempt was made.

From the change of impulse of a molecule rebounding from a moving piston he makes out an equation for adiabatic work, in the form

$$\Sigma A = v \cdot \Sigma\, 2n\,(c + v)\,.$$

Unfortunately he did not carry out the integration comprised in the command Σ. It is only qualitatively that he states on the basis of this equation "dass die geleistete Arbeit gleich der Abnahme der lebendigen Kraft der Moleküle ist".

VOIGT [5] is the first to set a definite aim at deducing the Poisson-correlation also from kinetical considerations. Unfortunately, influenced by the point of view of his age, he works with energy expressions instead of with the impulse theorem, and so uses a rather cumbersome method. He is also the first to apply kinetical considerations in the deduction of the laws of "Mariotte—Gay—Lussac", and "Poisson", for molecules with translational energy only (monatomic molecules). In his deduction we sensed the omission of just that, which seems to be the essence of this paper, i. e. that the correlations between the macro-movement of the piston and the micro-movements of the molecules be made vividly descriptive.

NATANSON [6] applies the kinetic theory to the expansion defined by Joule, and to the effusion of gases, but neither does he deal with adiabatic expansion.

In the very well known work of MEYER [7], which is extensively quoted even today, only the deduction of CLAUSIUS is reproduced on an energetical basis and he arrives at a formal expression of work

$$p \cdot \delta V = \frac{1}{3} F . N . mc^2 \cdot v$$

where F is the surface of the piston.

PAUL [8] uses kinetic consideration only in his treatment of quasi-adiabatic processes of work.

Among the handbooks, in that of JEANS [9] referred to by PARTINGTON, no mention is made of this idea; HERZFELD [10] is the only one who, citing CLAUSIUS [3, 4] and KRÖNIG [2], (and also starting from the law of conservation of energy) attempts the above deduction but in a somewhat individual manner. Postulating a "one dimensional gas" ("eindimensionales Gas") he arrives by a rather awkward process to the value

$$p V^3 = p_0 V_0^3$$

for this case, for when only one dimension is considered C_v would be equal to $\frac{1}{2} R$ and C_p would be equal to $\frac{3}{2} R$, that is $\varkappa = \frac{C_p}{C_v} = 3$. After this not readily acceptable abstraction he proceeds to a three dimensional gas. The deduction is formal and cumbersome even aside from the concept of a one dimensional gas, and there is no direct indication as to how an increase in temperature results from an increase in kinetic energy.

Thus, the foregoing seem to justify the surprising conclusion that a direct deduction of the functions of the adiabatic state, and of the equation of work, from a kinetic theory of gases, and based on the transfer of impulse, is not to be found in the literature of the past hundred years.

Summary

In the training of chemical engineers both a phenomenological and causal treatment of physical chemistry and chemical operations is current. The deduction of adiabatic compression, as presented here, shows that the essence of the process is better revealed by a causal explanation.

Starting from the hypothesis of Clausius concering the kinetic motion of gas molecules, and based on the law of transfer of impulses a rather simple and descriptive method is available for deducing the correlation stated by Poisson as

$$T \cdot V^{\varkappa = 1} = \text{Const.}$$

In spite of the fact that this point of view is obvious the deduction of this correlation based on the law of impulses, is not to be found in literature.

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