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THE WORKS OF RICHARD MOLLIER*

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FOREWORD

On the hundredth anniversary of the birth of Richard Mollier, a brief review of his published works and of the influence of these works upon the engineering profession is appropriate. We have attempted, in the paragraphs which follow, to provide such a review.

BIOGRAPHICAL SKETCH

Although a biographical sketch of Mollier is not the primary purpose of this paper, a brief review is provided in order to place his works in perspective. More detailed biographical information is provided in the one biography, the three necrologies and the five notices "Zum 70. Geburtstag" listed in Volumes VI and VIIa of *J. C. Poggendorffs biographisch-literarisches Handworterbuch*.

Richard Mollier was born in Triest on 30 November 1863, the oldest son of Eduard Mollier, director of the Triester Maschinenfabrik und Schiffswerft. His mother was the daughter of Carl von Dyck, director of the Königlich Bayerschen Eisenbahn. After passing with distinction the final examination at the Deutschen Gymnasium in Triest in 1882, Richard Mollier studied mathematics and physics for two years at the Universität, Graz, and Mechanical Engineering for four years at the Technische Hochschule, München. From 1888 to 1890, he worked as an engineer in his father's machine factory and shipyard. He returned then to München, where he served for two years as Assistant für Theoretische Maschinenlehre with Professor Moritz Schröter, at the end of which time he was admitted as Privatdozent. He was awarded the degree of Doktor der Philosophie three years later, in 1895.

He was called, in the fall of 1896, to the position of planmässiger ausserordentlicher Professor für angewandte Physik und Maschinenlehre at the Universität Göttingen; a year later, at the age of 33, he was called to the position of ordentlicher Professor für Technische Thermodynamik at the Sächsischen Technischen Hochschule in Dresden, succeeding Professor Gustav Zeuner. Here Mollier taught for 36 years until his retirement at the age of 69. He passed away two years later, after a very brief illness, on 13 March 1935.

As will be brought out in the paragraphs which follow, Richard Mollier's professional career was motivated largely by a desire to provide engineers with aids for the solution of difficult problems of thermodynamics, heat transfer and mass transfer; his success was due largely to his effective use of graphical methods. The concern for the engineer's problems may be traced to his family background; his effective use of graphical methods in thermodynamics appears to have roots in the works of J. Willard Gibbs and Gustav Zeuner. Gibbs' first two papers, [1, 2], were published originally in 1873 and translated by W. Ostwald into German in 1892 [3]; Zeuner's Thermodynamics texts [4] and [5] appeared respectively in 1860 and in 1890. Mollier's writings indicate a high respect for the effective use of graphical methods exhibited by these two thermodynamicists.

PUBLISHED WORKS

A chronological list of the published works of Richard Mollier known to the authors is appended as a Bibliography. Brief comments on these works follow.

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Mollier's first paper [B1], his Habilitationsschrift, clarifies and extends, for the benefit of the engineer, the use of the temperature-entropy diagram. Regarding Gibbs' first paper [1], he writes in the introduction, "In dieser Arbeit ist dem Entropie-Temperaturdiagramm ein eigenes Kapitel gewidmet und darin sind mit vollster Klarheit die allgemeinen Eigenschaften des Diagramms entwickelt und dessen grosse Verwendbarkeit auch für technische Zwecke betont". Also, commenting on Zuener's second text [5], he states "Bei weitem ausführlicher als alle bisher genannten Schriften beschäftigt sich mit dem Gegenstande Zeuner's *Technische Thermodynamik*, indem hier das Wärmediagramm fast durchgehends parallel mit dem Indikatordiagramm zur darstellung allgemeiner und technischer Probleme verwendet ist, und so bildete denn auch das Studium dieses Werkes, neben dem der früher genannten Schrift von Gibbs die hauptsächliche Grundlage zu der folgenden Arbeit". As further evidence of his appreciation of the value of graphical representations, we find the phrase "um es an zahlreichen Beispielen vor Augen führen", or its equivalent, used more than once. In an appendix, we find an interesting discussion of the use of co-ordinates (such as work) which are not unique functions of the thermodynamic state of the system; he suggests that such co-ordinates might be useful for the representation of certain processes, but that the use of state variables is preferred in general. (Incidentally, contrary to the impression given by Partington [6, p. 179], the enthalpy–entropy diagram is not mentioned in Mollier's first paper; the writers find it mentioned first in Mollier's 1904 paper). This first paper, written clearly and illustrated effectively with fourteen line drawings, sets the stage for all of his following technical publications. Although written 70 years ago, students of thermodynamics still would find this paper stimulating.

In his second publication [B2], graphical methods provide a simplified description of the relative motions of the slide valve and the piston in the steam engine. This paper, as well as nearly all of the papers which follow, appeared in the *Zeitschrift des Vereines deutscher Ingenieure*, an indication of his effort to reach the practising engineer.

His dissertation [B3], concerning the entropy of vapors, established further his reputation as a thermodynamicist. Unfortunately, this work does not appear to have been published in a form which is available readily. The writers have been unable to locate copies of this work.

Next, beginning with available thermodynamic data and using the general methods of thermodynamics, he expressed the thermal properties of CO_2, NH_3 and SO_2 in forms convenient for use by refrigeration engineers [B4]. Whenever possible, he uses, for CO_2, the data published by Amagat several years earlier. Temperature-entropy relations are presented in equation form for all three refrigerants, also in tabular form for CO_2 and NH_3, and also in graphical form for CO_2. He considered apparently CO_2 to be the most important and SO_2 the least important of these three refrigerants.

Motivated by the fact that a large portion of the processes occurring in CO_2 refrigerators involve superheated CO_2, and beginning with the experimental results of Amagat, he extended these tables and graphs in the following year to include superheated CO_2 [B5]. Numerical examples at the end of this paper illustrate the use of such tables and graphs and show that analytical results obtained using the given tables and graph are in better agreement with experimental results than are analytical results obtained using the calculation procedures of contemporary refrigeration engineers.

His review paper on heat transfer and related experimental results [B6] was prepared at the request of the VdI (Vereines deutscher Ingenieure). The VdI had appropriated, in 1895, 5000 M "für Arbeiten zur Lösung der Aufgabe betr. den Durchgang der Wärme durch Heizflächen" [7] and asked Mollier to provide a starting point for these studies by clarifying, on the basis of available research results, the state of understanding of the laws of heat transfer. In the resulting paper, conduction, convection and radiation (including convection with boiling and convection and radiation from flames) are discussed extensively. Most of the reviewed studies appear to have been motivated by the problems encountered in generating and handling steam. Although many of the fundamental concepts which are used today in heat transfer studies are mentioned in this paper, quantitive correlations were in the first stages of development. E.g. although the variation of the forced-convection unit conductance had been established as a function of the square root of the fluid speed (for low fluid speeds), no expression relating quantitatively the unit conductance with fluid properties and system geometry is given; again, although Stefan's radiation equation had been presented 8 years previously, it was not yet accepted universally. Mollier points out inconsistencies in some of the measurements, suggests possible sources of errors, and emphasizes the need for more extensive and more accurate data. He expresses the highest regard for the manner in which Joule arranged his experiments and drew his conclusions.

His paper on the evaluation of the steam engine [B7], in which he advocates comparing the measured thermal efficiency of the engine with the efficiency computed neglecting losses due to irreversible processes, was motivated by the fact that some engineers, including Zeuner, made a practice of comparing the measured thermal efficiencies of *all* steam engines, regardless of the cycle of operation, with the efficiency of a Carnot cycle operating between the same temperature limits. The procedure advocated by Mollier provided a more meaningful measure of the engine performance as influenced by its design and construction.

As further evidence of his desire to aid the practicing engineer, we find that he authored or co-authored for three decades the section "Wärme" in *Hutte, des Ingenieurs Taschenbuch* [B8]. (We have been able to establish with certainty that he authored this section in the 18th edition in 1902 and co-authored this section in the 26th edition in 1931 with F. Merkel.) The 21st (1911) and succeeding editions are divided into parts on thermal properties of materials, heat transfer, general laws of thermodynamics, perfect gases, vapors, flows of gases and vapors, and combustion. Numerous applications (power production, refrigeration, etc.) are discussed. Combining a sound understanding of the physical processes, the powerful methods of thermodynamics, and a desire to aid (rather than to impress) the engineer, he wrote so clearly that we find it necessary to remind ourselves that the earlier editions are over a half century old. We are especially impressed by the clarity of his discussion, in the earlier editions, of the maximum useful work which can be obtained from a closed system. The only place in which we would desire greater clarity is in his use of the word "adiabatic"; when Mollier writes "adiabatic", he means "constant-entropy", at variance with current usage. The fact that Mollier authored this section in *Hütte* explains perhaps why we do not find a thermodynamics textbook by Mollier; such a textbook might have duplicated much of the material in *Hütte*.

His paper on the gas force required at the piston head to accelerate the connecting rod [B9] was motivated by the wide variations in the assumptions made by designers when handling this problem. Skilfully combining analytical methods, graphical methods, engineering approximations and a survey of typical designs, he is led to recommend that the designer add half the mass of the connecting rod to the mass of the remaining reciprocating parts, a recommendation with simplicity and usefulness typical of Mollier.

His next paper, on the degree of irregularity of intermittent-firing internal-combustion engines with idle-stroke governing [B10], also was written in order to correct false concepts. Typical of Mollier, a clarifying graphical presentation of the results of his analysis is included.

His best-known publication is perhaps his paper on new diagrams for engineering thermodynamics [B11], appearing the year following Gibbs' death. He presents enthalpy–entropy diagrams for steam and for carbon dioxide, suggesting that these diagrams might be useful in studies of steam engines, steam turbines, steam jets, throttling processes, and refrigerators. In closing, he presents also an enthalpy–pressure diagram for carbon dioxide, suggesting that this diagram might be useful in studies of processes involving fixed pressure levels, such as occur in refrigerators.

His shortest paper is the two-sentence description of the geometrical relationship between the mass polygon and the distance diagram for a four-cylinder machine balanced to first approximation [B12]. It is accompanied, of course, by the appropriate diagram.

Mollier, recognizing the value of Callendar's state equation for steam, used it as the basis for his tables and diagrams for steam [B13] which appeared in 1906. Mollier's improved version of Callendar's equation was used in the later editions, the seventh edition appearing in 1932. Both an enthalpy–entropy diagram and an enthalpy–pressure diagram are included.

Equations and diagrams applicable to processes occurring in a gas generator are presented in Mollier's next paper [B14]. Because information required for the calculation of equilibrium compositions was not available at that time (1907), he used the first law of thermodynamics and the appropriate chemical equations to express, for the reaction of air and H_2O with coal, the H_2, CO and N_2 content of the generator products as functions of the CO_2 content of the products, the O_2 content of the incoming air and the generator efficiency. The fact that the CO_2 content (a measure of the extent of reaction) is left undetermined is a consequence of omitting the conditions for chemical equilibrium. He emphasizes explicitly the need for equilibrium-composition data.

The only non-technical writing by Mollier which we have found is the paper on Zeuner [B15] presented at the general meeting of the VdI in 1908, the year after Zeuner's death. The similarities of objectives and thought processes between Mollier and Zeuner, brought out by this paper, are remarkable. Mollier writes, concerning Zeuner's motivations, "Er hat eine Lebensaufgabe darin gefunden, die Maschineningenieure die Gesetze der mechanischen Wärmetheorie zu lehren" and, with regard to his methods,* "Zeuner denkt augesprochen geometrisch und erleichtert dem Leser die Auffassung überall durch Schaulinien". Mollier was truly Zeuner's successor!

For more than a decade after this paper, we find no new writings by Mollier. Although the cause for this publishing inactivity is not apparent at the distance from which we are examining his career, we suspect that World War I aggravated this inactivity.

His next publication, in 1919, was motivated once again by the desire to correct a popular misconception. During the preceding 15 years, several cycles in which pistons and rotors are replaced largely by nozzles had been proposed, and a Deutsches Reichspatent had been issued for a refrigerator in which the expansion and a portion of the compression take place in nozzles. Mollier examined both power and refrigeration cycles in which pistons and rotors are replaced, at least in part, by nozzles and showed [B16] that viscous losses render these cycles impracticable.

The only paper which Mollier published in a non-engineering journal bears on a graphical representation of the equation of state [B17], appearing in *Physikalische Zeitschrift.* His choice of co-ordinates (based upon an examination of van der Waals' equation of state) reveals, in graphical form, deviations from the van der Waals equation and provides, for several empirical expressions, a better physical understanding.

As a consequence of increasing interest in combustion processes, his 1907 paper on gas generation is extended in 1921 in a paper on the equations of the combustion process [B18]. For the case in which the combustion products consist only of O_2, N_2, CO and CO_2, he develops relationships between the amount and composition of the combustion products, the amount and composition of the fuel (solid, liquid or gaseous) and the amount of supplied air. As in the earlier study, the CO_2 content (a measure of the extent of reaction) is left undetermined. The paper improves upon an assumption made earlier by Ostwald regarding the relationship between the amount of excess supply air and the amounts of O_2 and CO_2 in the combustion products. This paper is unique among Mollier's twenty publications in that it contains no diagrams.

Mollier's enthalpy–mass fraction diagram for binary mixtures appears first in his paper presenting a new diagram for vapor–air mixtures [B19]. In this paper he suggests that the enthalpy–mass fraction diagram is more versatile than the enthalpy–temperature diagram in use

* Concerning the use of geometrical methods in thermodynamics, compare Mollier's comment on Zeuner with Bumstead's comment on Gibbs [8], "Professor Gibbs was much inclined to the use of geometrical illustrations, which he employed as symbols and aids to the imagination . . . and this method he used with great ease and power."

at that time. Such diagrams are used chiefly for situations in which one of the components cannot be treated as a perfect gas; Mollier's diagram is convenient especially for processes in which the composition does not vary. Relative to the psychrometric chart, his diagram has the advantage that the end state for mixing processes may be obtained exactly by simple geometrical constructions.

Improvements on this diagram are included in the paper on the *i,x*-diagram for steam–air mixtures [B20]. He recommends using inclined co-ordinates and replacing lines of equal relative humidity by lines of equal degree of saturation. The last section of this paper (the last paper published by Mollier) is perhaps his most controversial publication. He entered into the discussion of the theory of the psychrometer and assumed (as did Carrier) that the wet-bulb temperature equals the adiabatic-saturation temperature. Although this assumption is correct numerically, to a good approximation, for water diffusing into air over a wide range of flow conditions, it is not correct in principle; one must take into account, as shown by Busemann [9], Kirschbaum [10] and others (see e.g. Matz [11, p. 165] and Sherwood and Pigford [12, p. 97]), the pertinent transport phenomena. Unfortunately, many thermodynamics textbooks state, even today, that the wet-bulb temperature and the adiabatic-saturation temperature are equal.

If one examines the authorships of the twenty publications listed in the Bibliography, then one notices that (with the exception of the last edition of the "Wärme" section in *Hütte*) all of the publications were authored by Mollier alone. As a possible explanation, we note that Nägel writes [13], on the occasion of Mollier's 70th birthday, "Es verdient besonders hervorgehoben zu werden, dass es Mollier in erster Linie am Herzen lag, seine erfolgreichsten Probleme durch seine Assistenten bearbeiten zu lassen und diesen die volle Autórschaft für die erzielten Ergebnisse zuzuschreiben". This procedure was certainly a most generous policy on the part of a great engineer and educator!

We notice also that Mollier was, although extremely modest, confident of the value of his works. Nägel writes [14], "Obwohl er sich seines Könnens und seines Wertes wohl bewusst war, war doch immer die persönliche Bescheidenheit der Zug, der seinen Charakter hervorstechend auszeichnete". This modesty and confidence reminds us again of Gibbs, of whom Bumstead writes [8], "His modesty with regard to his work was proverbial among all who knew him, and it was entirely real and unaffected. There was never any doubt in his mind, however, as to the accuracy of anything which he published, nor indeed did he underestimate its importance. . . ."

PROFESSIONAL CONTRIBUTIONS AND RECOGNITION

The recognition awarded a man is not always proportional to his professional contributions; sometimes the recognition is disproportionately low (specially in the case of pioneers), many times it is disproportionately high (specially in the case of followers). The further we delve into the professional contributions of Mollier, the more we are convinced that his contributions are more valuable than is appreciated generally, especially by the younger engineers in the United States.

As a lower limit to the value of these contributions, let us summarize briefly the highlights of the recognitions given Mollier. At the age of 33, he was called to the position of ordentlicher Professor für Technische Thermodynamik, i.e. his contributions and potential in the field of thermodynamics were recognized early. In 1919, the Technische Hochschule in Braunschweig conferred upon him the degree Ehrendoktor. In 1928, the VdI awarded him its highest honor, the Grashof Medal, in recognition of his contributions, as an outstanding teacher and investigator, to the development of engineering thermodynamics for the purpose of understanding thoroughly the processes in heat-power and refrigeration machines. His tables and diagrams for steam [B13] and his last two papers [B19 and B20] were translated and published in the English language [15–17]. At the time of his 70th birthday, he was honored by articles in *Forschung auf dem Gebiete des Ingenieurwesens*, *Zeitschrift für die gesamte Kälte-Industrie*, *Forschungen und Fortschritte*, and *Zeitschrift für angewandte Mathematik und Mechanik*; an issue of *Forschung auf dem Gebiete des Ingenieurwesens*, as well as *Forschungsheft 363*, prepared by his students and colleagues, was dedicated to him; Busemann dedicated his volume on *Der Wärme- und Stoffaustausch dargestellt im Mollierschen Zustandsdiagramm für Zweistoffgemische* [9] to Mollier; and a *Festschrift* was published, at Karlsruhe, in his honor. At the time of his death, necrologies appeared in *Zeitschrift des Vereines deutscher Ingenieure* (in which journal he published nearly all of his papers), in *Zeitschrift für die gesamte Kalte-Industrie* (in which journal he published two of his earlier papers) and in *Sitzungsbericht Isis Dresden.* On 26 May 1936, the directorate of the VdI, at the suggestion of the Ausschusses für Wärmeforschung and the Deutschen Kältevereins, resolved that the *i,s*-, *i,p*- and *i,x*-diagrams should henceforth be known as Mollier diagrams and be identified respectively as the Mollier-*i,s*-Diagram, the Mollier-*i,p*-Diagram and the Mollier-*i,x*-Diagram.* Because his professional career was motivated largely by a desire to provide engineers with aids for the solution of difficult problems of thermodynamics, heat transfer and mass transfer, the recognitions by the several engineering societies are significant indeed; he employed graphical methods so effectively that the association of his name with these three graphs is certainly appropriate.

The influences of Mollier on current technology, consisting of both tangible and intangible influences, is difficult to evaluate. In the paragraphs which follow, we can hope to touch briefly upon only a few of the most obvious contributions.

Consider first the more tangible influences. In spite of the fact that the engineering problems of Mollier's time have been replaced, to a large extent, by new engineering problems, the thermodynamic diagrams and parameters introduced by Mollier are still in use today. Regarding the Mollier-*i,s*-Diagram, Keenan writes [22, p. 88], "The enthalpy–entropy chart is probably the chart most commonly employed as an aid in engineering calculations. It is called the Mollier chart in honor of Richard Mollier, who first proposed its adoption". Used primarily for imperfect gases, it has served specially engineers dealing with processes involving steam and recently engineers dealing with processes involving relatively high temperatures. For a recent steam application, see the diagram prepared by Schmidt [23]; as examples of high-temperature applications, see the diagram prepared by Feldman [24] for air up to 13 000°K, for use in hypersonic-flow problems, and the diagram prepared by Ducati [25] for helium up to 46 000°K, for use in plasma-flow problems. The Mollier-*i,p*-Diagram, used widely in the refrigeration industry, is used frequently now also in applications involving cryogenic fluids and high-temperature gases. For examples of cryogenic-fluid applications, see, e.g. Scott [26]; as an example of high-temperature applications, see the diagram prepared by Moeckel and Weston [27] for air up to 15 000°K. The Mollier-*i,x*-Diagram continues to be used widely for humidifying, evaporative-cooling, drying and similar processes occurring, e.g. in the fields of air conditioning, chemical engineering and meteorology; see, e.g. Eckert and Drake [28, Ch. 15]. The gas-generator diagram included, e.g. by Bošnjaković [18, p. 225] has its origin in Mollier's paper [B14], whereas the combustion parameters used, e.g. by Schmidt [29, p. 239] come from Mollier's 1921 paper [B18]. The availability-entropy diagram published by Keenan [30] was derived from the Mollier-*i,s*-Diagram. The writers suggest that a diagram in which the available-energy function (suggested by Evans [31] as a generalization of Keenan's availability) is displayed as a function of entropy might prove to be a useful diagram in the field of thermo-economics.

Consider now the less tangible influences. Foremost among these contributions is perhaps his direct influence upon immediate associates and students—some of whom are still practicing engineering. Nägel writes [14], "Er wies ihnen

* Sometimes several other thermodynamic-state diagrams either are credited to Mollier or are called Mollier Diagrams. E.g. Bošnjaković credits Mollier with the *i*-log *p* diagram [18, p. 135] and with the *i-T* diagram [19, p. 15] whereas Tribus calls the *T-s* diagram a Mollier Diagram [20, pp. 281 and 285]. However, Callendar suggested apparently the *i*-log *p* diagram [21, p. 353] whereas Mollier credits O. H. Mueller with suggesting the *i-T* diagram [B19] and Belpaire with suggesting the *T-s* diagram [B1].

nicht nur die Bahnen der gedanklichen Förderung schwebender wissenschaftlicher Probleme, er lebte ihnen ein Vorbild vor, das einen Reichtum an wertvollsten Motiven für die Formung des eigenen Lebens darbot". The extent to which these associates and students propagated the values received from their contacts with Mollier will never be known. Additional intangible influences derive from his published works—paragons of modesty and directness, and evidences of powerful thought processes and benevolent motivations—inspirations for generations to follow.

CLOSING REMARKS

This review was undertaken as a challenge—to discover what could be done in a short time and with materials available in the United States libraries (chiefly in the University of California libraries) and in our private libraries. We trust that this brief and incomplete evaluation of Richard Mollier and his works will emphasize the human side of engineering contributions, a side which is overshadowed too often by the inanimate side.

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