

# A TRANSFORMATION OF THE MOLLIER $i \sim x$ DIAGRAM

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**Abstract**—A new enthalpy-composition diagram is presented for steam-air-water mixtures; it combines the advantages of the Mollier  $i \sim x$  diagram with those of the diagram having mass-of-mixture as the reference quantity, and avoids some of the disadvantages possessed by those diagrams. The new diagram is akin to that having moles-of-mixture as the base, but “artificial” molecular weights are used: that of air is taken as twenty-five times that of water.

It is shown that most of the usual graphical procedures for calculating heat and mass transfer remain valid on the new diagram, without any modification. The small amendments required by a minority of the constructions are described.

## NOMENCLATURE

Concentration variables:

- $f_2$ , mass of H<sub>2</sub>O per mass of mixture;  
 $f_1$ , “noles” of H<sub>2</sub>O per “nole” of mixture;  
 $x$ , mass of H<sub>2</sub>O per mass of dry air.

Enthalpy variables:

- $h$ , enthalpy per mass of mixture;  
 $\bar{h}$ , enthalpy per nole of mixture;  
 $i$ , enthalpy per mass of dry air.

Also:

- $B$ , dimensionless mass-transfer driving force;  
 $g_{GC}/U$ , dimensionless ratio of heat-transfer conductance on gas side of interface to heat-transfer conductance on liquid side of interface;  
 $N_G$ , number of gas-side transfer units.

## 1. INTRODUCTION

NOT the least of Mollier's achievements was his introduction of diagrammatic representations of thermodynamic properties, which have been found by engineers to facilitate the understanding and execution of some important calculations. The two best-known of these are, of course, the enthalpy-entropy diagram for steam, and the enthalpy-composition diagram for steam-air mixtures. The present paper concerns the second of these [1].

In a booklet dedicated to Mollier on the

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occasion of his seventieth birthday, Busemann [2] clearly showed that Mollier's  $i \sim x$  diagram could be regarded as a member of a family of diagrams; the characteristic of this family was that any member diagram could be derived from any other member diagram by central projection. Busemann also showed how constructions carried out on Mollier's  $i \sim x$  diagram could yield quantitative information about the rates of heat and mass transfer in the vicinity of water-air interfaces.

Busemann's results were independently derived and extended in a much later paper by the present author [3]; that paper exploited some of the possibilities of diagram construction implicit in the projective properties of the situation and also contained fairly general formulae by which the heat- and mass-transfer manipulations valid for one diagram could be made valid for another member of the family.

The aim of the present paper is more modest: it is to describe one particular enthalpy-composition diagram, valid for air-steam mixtures at a pressure of 1 atm, which is particularly suitable for the graphical solution of the problems arising in drying, air-conditioning, and cooling-tower practice.

## 2. THE NEW ENTHALPY-COMPOSITION DIAGRAM

### 2.1 Some properties of Mollier's diagram

Mollier's enthalpy-composition diagram has as abscissa quantity  $x$ , the mass of H<sub>2</sub>O per mass

of dry air; the ordinate quantity is correspondingly  $i$ , the enthalpy of the mixture, per mass of dry air, so defined that  $i = 0$  for both water and air at 32°F. Incidentally, lines of constant  $i$  are drawn so as to cut lines of constant  $x$  obliquely rather than at right angles; however this is of no relevance here.

A consequence of the reference of mixture properties to the mass of dry air contained in the mixture is that state-points representative of pure H<sub>2</sub>O lie at infinity; correspondingly, state-points for mixtures having a high H<sub>2</sub>O/air ratio lie beyond the edge of any diagram which adequately represents the region of slightly moist gas. The absence of the "pure-H<sub>2</sub>O" line complicates the graphical procedures of transfer-rate calculation, and also necessitates some imaginative effort from the user.

On the other hand, the  $i \sim x$  co-ordinate system permits the clear representation, to as large a scale as is desired, of the technically important mixtures having only low moisture content.

## 2.2 Other known diagrams

Most enthalpy-composition diagrams which are used in technical calculations refer both enthalpy and composition to the total mass or to the number of moles of the mixture (see, for example, [4]). The former practice has been used for H<sub>2</sub>O-air mixtures by the present author [5]; the latter has been used for such mixtures by Bošnjaković [6].

These practices permit the whole range of physically realizable mixtures to be represented by a concentration variable (mass fraction, or mole fraction) which varies between zero and unity. Then both the "pure-air" and "pure-H<sub>2</sub>O" conditions appear as real lines on the diagram; graphical rate calculations are eased, and less is left to the imagination.

The fractional concentration of H<sub>2</sub>O in many technically important situations is of the order of a few per cent, whether on a mass or a mole basis; consequently, the corresponding state-points are confined to a rather small area on the diagram, a fact which hampers accurate graphical calculations. The advantage of having an accessible "pure-H<sub>2</sub>O" line has thus been bought at the cost of eye-strain and inaccuracy.

## 2.3 A diagram based on fictitious molecular weights\*

A diagram will now be described which possesses the advantages and avoids the disadvantages just described, i.e. one for which all real-mixture compositions are represented by numbers in the range from 0 to 1, yet for which the region of slightly moist mixtures occupies a large fraction of the diagram area. It is most simply approached by way of the following argument:

When mole-based diagrams are used, the mass unit of reference is 29 lb for pure air, 18 lb for pure H<sub>2</sub>O, and some intermediate value for a mixture. These numbers have been used historically because of the relative weights of the molecules in question; yet molecular properties are quite irrelevant to the questions in hand. Therefore *any* pair of mass units can be used; and this pair can be chosen so as to give the resultant diagram a convenient shape.

Let us define "1 nole" of H<sub>2</sub>O as 1 lb of H<sub>2</sub>O, and "1 nole" of air as 25 lb of air.† Then a mixture of  $x$  lb of H<sub>2</sub>O with 1 lb of air will contain  $(x + 1/25)$  "noles"; and the "nole fraction" of H<sub>2</sub>O in the mixture, to which we ascribe the symbol  $\tilde{f}$ , will be given by:

$$\tilde{f} = \frac{x}{(x + 1/25)} \quad (1)$$

Obviously,  $\tilde{f}$  equals zero for dry air, and  $\tilde{f}$  equals unity for pure water, so all real mixtures have  $\tilde{f}$  values lying between 0 and 1. For slightly moist mixtures ( $0 < x < 0.2$ ),  $\tilde{f}$  is considerably greater than  $x$ , indeed almost twenty-five times as great for very small  $x$ .

Fig. 1 is a diagram having the "nole of mixture" as the reference quantity, both for the composition and for the enthalpy. The abscissa quantity is accordingly  $\tilde{f}$ ; and the ordinate quantity is  $\tilde{h}$ , the enthalpy per "nole" of mixture, so defined that  $\tilde{h}$  equals zero for both air and water at 32°F. The lines drawn are the isotherms

\* The idea of a fictitious molecular weight is here used solely as a convenient introductory device. It plays no part in the justification of the final results.

† The term "nole" is used here because, being both like and unlike "mole", it may aid understanding. The term is, however, inessential to the argument and, if unhelpful, should be ignored.

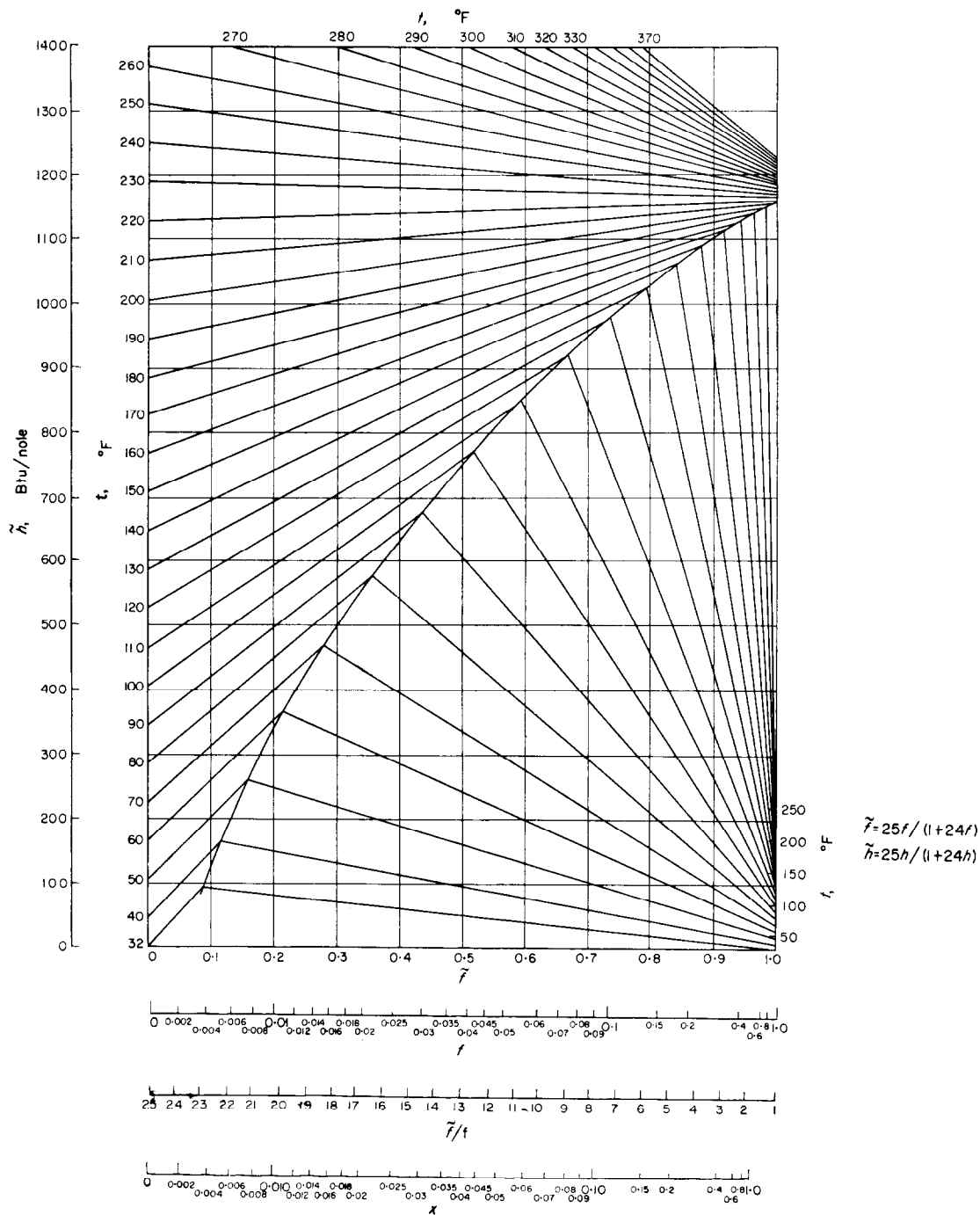


FIG. 1. Enthalpy-composition diagram for H<sub>2</sub>O-air at 1 atm pressure. Mass unit is "1 nole" where, 1 nole of H<sub>2</sub>O ≡ 1 lb, 1 nole of air ≡ 25 lb.

and the saturated-vapour curve for 1 atm pressure. It is this diagram which is here recommended as particularly convenient for the solution of heat- and mass-transfer problems arising in drying, air-conditioning, etc. Of course it is only one of many possible diagrams; thus we could with almost equal advantage have defined 1 "nole" of air to consist of 20 lb or 30 lb of air.

The diagram is provided with horizontal scales of  $x$ ,  $f$  and  $\tilde{f}/f$ . The first of these permits easy comparison with Mollier's  $i \sim x$  diagram; evidently the "slightly moist" mixtures ( $x$ -values of a few per cent) lie squarely in the middle of the diagram. The second quantity stands for the mass of  $H_2O$  per mass of mixture; it is related to  $\tilde{f}$  by:

$$\tilde{f} = \frac{25f}{(1 + 24f)} \quad (2)$$

As a consequence,

$$\frac{\tilde{f}}{f} = 25 - 24\tilde{f} \quad (3)$$

So the  $\tilde{f}/f$  scale is a linear one, which is useful for interpolation.

Incidentally, the following equations connect the various enthalpies, as may easily be shown:

$$\tilde{h} = h \cdot \frac{\tilde{f}}{f} = \frac{i}{x + 1/25} \quad (4)$$

#### 2.4 The use of the new diagram

It is clear that the diagram illustrated in Fig. 1 does superficially combine the advantages of the Mollier diagram and of the mass- or mole-based diagrams. However, a further question remains: can a diagram so constructed serve *all* the purposes to which more conventional diagrams are put? The answer to the question may not be the same for each of the said purposes; we therefore list some representative ones as follows:

(i) Deduction of a third state property (e.g. enthalpy to any base) when two other properties are specified (e.g. temperature, and composition).

(ii) Calculation of the dew-point temperature or the wet-bulb temperature corresponding to a specified mixture.\*

\* These properties are distinguished, perhaps arbitrarily, from those referred to in (i) by the fact that their measurement involves the creation of different states from those of the mixture.

(iii) Calculation of the mass-transfer driving force given the states of the gas mixture in the bulk of the gas and at the water-air interface.

(iv) Determination of the interface condition when the bulk-gas and bulk-liquid states, and the corresponding conductances, are given.

(v) Determination of the direction and magnitude of the change in bulk-gas state which corresponds to a given interface state and a given increment in the number of gas-side transfer units.

With regard to item (i), the answer is affirmative, and results from the fact that there is a one-to-one correspondence between points on, say, the  $i \sim x$  plane and points on the  $\tilde{h} \sim \tilde{f}$  plane. For every point on the chart, the quantities  $t$ ,  $\tilde{h}$ ,  $\tilde{f}$  and so  $h$ ,  $f$ ,  $i$ ,  $x$ , etc., can be determined by inspection of, and interpolation in, the appropriate scales.

As to item (ii), we must distinguish two parts; it is clear that a vertical line from the state-point in question to the saturated-gas curve will cut that curve at the dew-point temperature, since a vertical line is one of constant composition on the  $\tilde{h} \sim \tilde{f}$  diagram as well as on the  $i \sim x$  and the  $h \sim f$  diagrams (Fig. 2). On the other hand, to determine the wet-bulb condition, it suffices on the  $i \sim x$  or  $h \sim f$  planes to draw a line through the state-point so as to coincide with a mixed-phase isotherm, the temperature of which is the wet-bulb temperature.† When this construction is executed on the  $\tilde{h} \sim \tilde{f}$  diagram, as also shown in Fig. 2, it requires to be *proved* that the mixed-phase isotherm so found is still that corresponding to the wet-bulb temperature. Now on the  $i \sim x$  or  $h \sim f$  planes the mixed-phase isotherm, when produced, passes through the state-point G; so the desired result would certainly follow if every straight line on the  $i \sim x$  or  $h \sim f$  planes were to transform into a straight line on the  $\tilde{h} \sim \tilde{f}$  plane. We shall shortly see that the transformations *do* possess this property. It follows that the construction yielding the wet-bulb temperature *is* the same, whichever diagram is used.

One part of the answer relating to item (v) can be proved in the same way. On an  $h \sim f$  or  $i \sim x$

† We assume here and throughout that the Lewis number is unity so that this simple procedure is valid [5].

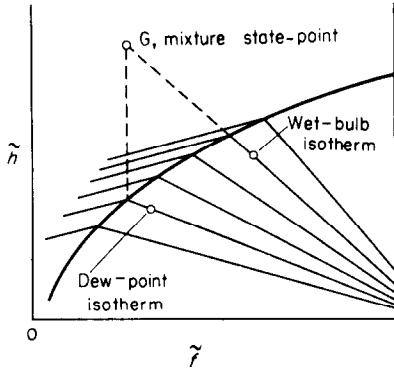


FIG. 2. Determination of dew-point and wet-bulb temperatures by means of graphical constructions on an  $\tilde{h} \sim \tilde{f}$  diagram.

diagram, the bulk-gas state-point shifts as a result of the heat- and mass-transfer processes from G to a nearby point  $G^+$  such that  $GG^+$  is collinear with the state-point S corresponding to saturated gas in contact with the liquid surface (and also collinear with the state-point T representing the "transferred substance" [5]). If straight lines remain straight on transformation, the direction of the line  $GG^+$  is determined in the same way on the  $\tilde{h} \sim \tilde{f}$  plane (Fig. 3).

Whereas the above constructions involve only the directions of lines, items (iii) and (v) involve length ratios. Thus the dimensionless driving force for mass transfer B is given by the equation:

$$B = \frac{\overline{GS}}{\overline{ST}} \quad (5)$$

when the lengths  $\overline{GS}$  and  $\overline{ST}$  are measured on the

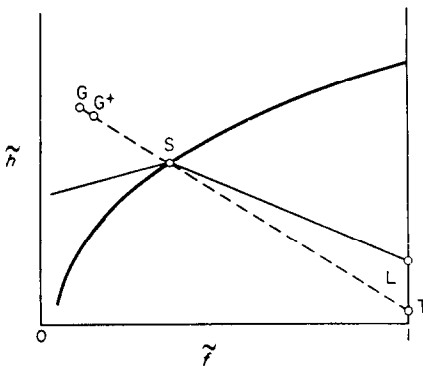


FIG. 3. Determination of the direction of shift of the bulk-gas state-point, from G to  $G^+$  for a Lewis number of unity. Note that the magnitude of the shift is given by equation (9).

$h \sim f$  diagram (Fig. 4). Similarly, the interface state is determined in terms of the conductance ratio  $g_{GC_F}/U$  by use of the construction also shown in Fig. 4, where:

$$\frac{U}{g_{GC_F}} = \frac{\overline{GA}}{\overline{AO}} \quad (6)$$

The explanations of these relationships can be found in [5]; it suffices for present purposes to note that length ratios make their appearance in graphical heat- and mass-transfer calculations. Since the  $\tilde{h} \sim \tilde{f}$  diagram is certainly not geometrically similar to the  $h \sim f$  diagram, we can be sure that equations (5) and (6) will not be valid when the lengths are measured in the  $\tilde{h} \sim \tilde{f}$  plane. What changes should be made?

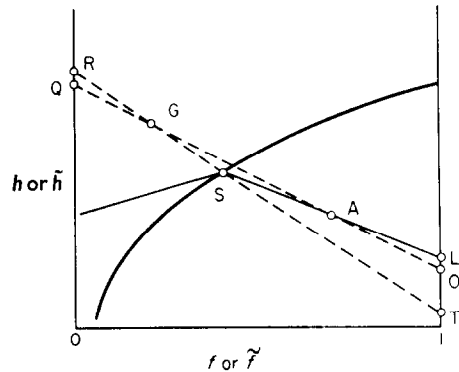


FIG. 4. Constructions on  $h \sim f$  or  $\tilde{h} \sim \tilde{f}$  diagrams relating to the determination of the mass-transfer driving force [equation (5) or (13)] and to the interface conditions [equations (6) or (14)].

The same question arises in relation to the magnitude of the shift of bulk-gas state  $\overline{GG^+}$ . It is shown in [8] that, on the  $h \sim f$  diagram, this length is related to the increment in the number of gas-side transfer units  $\delta N_G$  by:

$$\delta N_G = \frac{\overline{GG^+}}{\overline{G+S}} \cdot \frac{\overline{ST}}{\overline{GT}} \quad (7)$$

Will this relation still be valid when the lengths are measured on the  $\tilde{h} \sim \tilde{f}$  diagram?

These questions can be answered by making use of the theory of central projection, as is indicated in the next section.

### 3. DEDUCTIONS FROM PROJECTIVE GEOMETRY

#### 3.1 The projective relationship between the diagrams

It is shown in [3] that the transformations between the  $i \sim x$ ,  $h \sim f$  and  $\tilde{h} \sim \tilde{f}$  planes represented by equations (1), (2) and (3) are *homographic* ones; this means that a diagram on one of the planes can be derived from a diagram on another of them by central *projection*. Of course it was Busemann [2] who first demonstrated this, for the case of the  $i \sim x$  and  $h \sim f$  planes alone.

Fig. 5 illustrates one aspect of the relationships between the diagrams. The lines marked  $x$ ,  $f$  and  $\tilde{f}$  represent the baselines of an  $i \sim x$ , an  $h \sim f$  and an  $\tilde{h} \sim \tilde{f}$  diagram respectively; these diagrams are to be thought of as standing normal to the paper so that they share a common edge (enthalpy axis) running normal to the paper through the point  $O$ , where  $x = f = \tilde{f} = 0$ .  $P$  is an arbitrary point which has been chosen as the centre of projection; after its choice, the inclinations and lengths of the  $x$ ,  $f$ , and  $\tilde{f}$  scales have been chosen so as to satisfy equations (1) and (2). Obviously therefore the  $x$  scale must be *parallel* to the straight line which runs from  $P$  through the  $\tilde{f} = 1$  and  $f = 1$  points; and the distance from  $P$  to  $f = 1$  must be twenty-five times as large as the distance from  $P$  to  $\tilde{f} = 1$ . Inspection of Fig. 5 should make clear that Mollier's  $i \sim x$  diagram can be regarded as a shadow cast by an  $\tilde{h} \sim \tilde{f}$  diagram; or vice versa, of course.

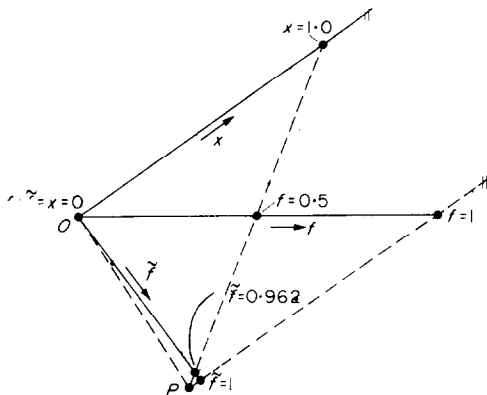


FIG. 5. The projective relationships between the  $i \sim x$ ,  $h \sim f$  and  $\tilde{h} \sim \tilde{f}$  diagrams.

#### 3.2 Straight lines remain straight

The shadow of a straight stick on a plane wall is itself straight; in other words, straight lines transform into straight lines when the transformation is homographic. This fact supplies the proof, anticipated in Section 2.4, for the validity of the usual graphical constructions for finding the wet-bulb condition and the direction of change of bulk-gas state, when these are carried out on the  $\tilde{h} \sim \tilde{f}$  diagram.

#### 3.3 The invariance of cross-ratios

If four points, A, B, C and D lie on a straight line (in any order), and this line is transformed homographically, the "shadows" of the points being A', B', C', D' respectively, a fundamental theorem of projective geometry yields [3]:

$$\frac{\overline{AB}}{\overline{AD}} \cdot \frac{\overline{CD}}{\overline{CB}} = \frac{\overline{A'B'}}{\overline{A'D'}} \cdot \frac{\overline{C'D'}}{\overline{C'B'}} \quad (8)$$

The expressions on the left and right of (8) are known as *cross-ratios*; the equation asserts that the magnitude of a cross-ratio is invariant to homographic transformations.

We now use this fact to prove that equation (7) holds, i.e. that the construction for the increment in the number of transfer units is valid, whether the construction is performed on the  $h \sim f$ ,  $\tilde{h} \sim \tilde{f}$ , or  $i \sim x$  diagrams. It suffices to observe that the expression on the right of (7) is a cross-ratio, as may be recognized by re-arranging it so that the letters fall in the same order as those in the expressions of (8); thus:

$$- \delta N_G = \frac{\overline{G+G}}{\overline{G+S}} \cdot \frac{\overline{TS}}{\overline{TG}} \quad (9)$$

It remains to modify the constructions for the driving force and for the determination of the interface state, i.e. to express equations (5) and (6) in forms valid also for the  $\tilde{h} \sim \tilde{f}$  diagram. This may be done by introducing reference to the points Q and R lying on the left-hand boundary of the  $h \sim f$  diagram of Fig. 4.

Equation (5) can be re-written as:

$$B = - \frac{\overline{GS}}{\overline{GR}} \cdot \frac{\overline{TR}}{\overline{TS}} \cdot \frac{\overline{GR}}{\overline{TR}} \quad (10)$$

But  $\overline{GR}/\overline{TR}$  is obviously equal to  $f_G$ ; so equation (10) becomes:

$$\frac{B}{f_G} = - \frac{\overline{GS}}{\overline{GR}} \cdot \frac{\overline{TR}}{\overline{TS}} \quad (11)$$

Similarly, equation (6) can be re-written as:

$$\frac{U}{g_{GC}F} \cdot \frac{1}{f_G} = - \frac{\overline{GA}}{\overline{GQ}} \cdot \frac{\overline{OQ}}{\overline{OA}} \quad (12)$$

Now the expressions on the right-hand sides of (11) and (12) are cross-ratios; they therefore have the same numerical values whether measured on the  $\tilde{h} \sim \tilde{f}$ ,  $\tilde{h} \sim \tilde{f}$  or  $i \sim x$  diagrams. Equations (11) and (12) are therefore generally valid, unlike (5) and (6) which hold only for the  $h \sim f$  plane.

Let us now suppose that the constructions are carried out on the  $h \sim f$  planes. It is easy to reverse the above argument and conclude that, in this case:

$$B \cdot \frac{\tilde{f}_G}{f_G} = \frac{\overline{GS}}{\overline{ST}} \quad (13)$$

$$\frac{U}{g_{GC}F} \cdot \frac{\tilde{f}_G}{f_G} = \frac{\overline{GA}}{\overline{AO}} \quad (14)$$

These equations represent the desired modifications to equations (5) and (6); equally, they indicate how the constructions for the local mass-transfer rate and for the interface-state determination must be carried out on the  $\tilde{h} \sim \tilde{f}$  diagram. All that is required is the introduction of the quantity  $\tilde{f}_G/f_G$ ; this varies in a linear fashion with the abscissa, as has already been noted.

#### 4. CONCLUSIONS

(i) The diagram shown in Fig. 1, having co-ordinates defined by equations (2) and (4), is convenient for heat- and mass-transfer calcu-

lations involving slightly moist gases such as arise in drying, air-conditioning, etc. The region of practically-occurring mixtures occupies a large fraction of the diagram area, but the diagram still possesses a line representing pure  $H_2O$ , for use in constructions for the mass-transfer driving force, for interface-state determination, for the shift of bulk-gas state, etc.

(ii) Most of the constructions normally carried out on  $i \sim x$  or  $h \sim f$  diagrams can be validly performed without modification on  $\tilde{h} \sim \tilde{f}$  diagrams such as Fig. 1. Where length ratios are involved however, the quantity  $\tilde{f}/f$  must be introduced into the relevant equations. To take the most important examples, equations (13) and (14) hold for the  $\tilde{h} \sim \tilde{f}$  diagram, in place of equations (5) and (6) which are valid for the  $h \sim f$  diagram. Equation (9), for the increment in the number of gas-side transfer units, is valid whichever diagram is used.

(iii) Although only one example has been considered, the principles invoked and techniques used in the present paper can be applied very widely. Thus their employment may facilitate the construction of diagrams for systems involving chemically reacting mixtures, and ablating substances, (e.g. [7]).

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**Résumé**—On présente ici un nouveau diagramme enthalpique pour des mélanges air-eau-vapeur; il allie les avantages du diagramme de Mollier  $i-x$  à ceux qui utilisent pour quantités de référence les masses de mélange et évite certains des inconvénients de ces diagrammes. Ce nouveau diagramme est équivalent à ceux qui prennent pour base les moles de mélange, mais utilise des poids moléculaires "artificiels": on prend pour l'air vingt cinq fois celui de l'eau.

On montre que la plupart des processus graphiques habituels de calcul de transfert de chaleur et de masse restent valables sans modification sur le nouveau diagramme. Les petits amendements nécessités par une minorité de constructions sont décrits.

**Zusammenfassung**—Für Dampf-Luft-Wasser-Gemische wird ein neues Enthalpie-Zusammensetzungs-Diagramm mitgeteilt; es verbindet die Vorteile des Mollier  $i$ - $x$  Diagramms mit denen jener Diagramme, die die Gemischmasse als Bezugsgröße haben, und vermeidet einige Nachteile dieser Diagramme. Das neue Diagramm ist mit jenem verwandt, das auf Mole der Mischung bezogen ist, jedoch werden „künstliche“ Molekulargewichte benutzt: das der Luft ist gleich dem fünfundzwanzigfachen von Wasser angenommenen.

Es wird gezeigt, dass die meisten der üblichen graphischen Verfahren zur Berechnung des Wärme- und Stoffaustausches ohne Änderung beibehalten werden können. Die geringen Abweichungen für einige wenige Konstruktionen werden beschrieben.

**Аннотация**—Описывается новая диаграмма энтальпия-состав для смесей водяной пар-вода-воздух. Она сочетает преимущества  $i \sim x$  диаграммы Молье и диаграммы, где в качестве исходной величины берется масса смеси, и исключает некоторые недостатки обеих. Новая диаграмма аналогична основанной на применении мольного состава смеси. Кроме того в ней используется понятие «условного» молекулярного веса. Для воздуха, например, он в двадцать пять раз выше, чем для воды.

Показано, что при построении новой диаграммы можно использовать большинство обычных графических методов расчета тепло- и массообмена без каких-либо видоизменений. Описаны некоторые изменения, необходимые для отдельных построений.