Int. J. Heat Mass Transfer. Vol. 16, pp. 371–384. Pergamon Press 1973. Printed in Great Britain

NEW FORMULATIONS OF THE CORRESPONDING STATES PRINCIPLE FOR THE TRANSPORT PROPERTIES OF PURE DENSE FLUIDS

K. LUCAS

Institut für Thermo- und Fluiddynamik, Technische Ruhr-Universität Bochum, W. Germany

(*Received* 17 *January* 1972)

Abstract—The usual formulations of the corresponding states principle are restricted to groups of similar substances. This can be understood from their common theoretical basis which is a very idealized molecular gas model. In this paper, a new approach to develop formulations of the corresponding states principle without this limitation is presented for the transport properties of pure dense fluids, viscosity and thermal conductivity. The theory is based on the concept of a point of correspondence, that is a universally distinguished point on the transport property surface at which a universal behavior of the transport properties is shown to exist for all fluids. On this basis, the reduced transport property at the temperature of the point of correspondence becomes a universal function of reduced pressure. This theoretical result is verified for several fluids which could not be forced into a common correlation by all earlier efforts. The universal result for one isotherm is generalized using the residual concept for transport properties.

NOMENCLATURE

TP,	general symbol for a transport property;
η	viscosity;
λ,	thermal conductivity;
T,	temperature;
p,	pressure;
ρ,	density;
R,	universal gas constant;
N_L,	Loschmidt number;
M,	molecular weight;
P,	point on a thermodynamic surface;
A_ν,	Taylor expansion coefficient;
f,	symbol for functional relation.

Subscripts

u,	universal;
R,	reduced;
cr,	critical;
0,	dilute gas.

Superscripts

$+$,	dimensionless;
ρ,	depending on density;
p,	depending on pressure.

1. INTRODUCTION

NUMERICAL values for the transport properties of fluids are essential to all problems involving heat and mass transfer. For pure fluids, viscosity and thermal conductivity have the greatest practical importance whereas self-diffusivity is predominantly of theoretical interest.

In the case of dilute gases, rigorous kinetic theory can be used to predict the transport coefficients. The calculated values agree well with experimental results as long as the limitations of the theory are observed. For dense gases and liquids, a reliable molecular theory of transport phenomena is still lacking.

An approach, entirely different from molecular theory, is based on the observation, that generalized equations can be formulated for the thermodynamic and transport properties of fluids, if all variables are written as dimensionless groups. The resulting equations or charts are valid for different fluids alike, they are not restricted to individual substances. The basis of this observation is called the corresponding states principle (CSP).

The statement of this principle, applied to a transport property, e.g. viscosity, as a function of temperature and pressure, can be written as:

$$\eta^+ = f_u(T^+, p^+) \qquad (1)$$

where η^+ is a dimensionless viscosity, T^+ and p^+ a dimensionless temperature and a dimensionless pressure respectively. The symbol f_u denotes a functional relation, which, if a formulation in accord with the objective of the principle has been found, is universal for all substances. For thermal conductivity, the analogous relation is:

$$\lambda^+ = f_u(T^+, p^+) \qquad (2)$$

where λ^+ is a dimensionless thermal conductivity and the other symbols have the same meaning as above.

If the quantities which are used to write the variables in dimensionless form are known for all fluids and if the function f_u has been evaluated from experimental values for one single substance, the transport properties of all other fluids may be calculated as a function of temperature and pressure from equations (1) and (2). This reveals the practical application of the corresponding states principle. Unknown properties of one fluid may be calculated from those known for another. The principle of corresponding states does not make any restrictive statement about the quantities which are used to write the variables in dimensionless form. The reduction with critical properties is most widely used. Other properties of the fluid, however, may also be chosen, the basic statement of the corresponding states principle being independent of that. The region of validity as well as the form of the function f_u are not defined either. For different reduction quantities f_u will be different, too.

This indetermination has led to numerous different formulations of the corresponding states principle. They differ from each other by the choice of the reduction parameters, the form and region of validity of the function f_u and in some cases by additional empirical parameters which have been introduced to improve the correlation.

2. THE PRESENT STAGE OF RESEARCH

None of the known formulations of the corresponding states principle satisfies its basic objective in general and in the total region of thermodynamic states. The functional relations between the dimensionless variables are not universal. They are restricted to groups of similar substances in more or less extended regions of state.

This limitation is due to the basic molecular model which is common to all correlations of that kind. This model assumes simple molecules without the influence of internal degrees of freedom and quantum effects as well as a universally valid potential function. In reality, only very few substances conform to such restrictions. Relations which have been deduced from these assumptions by dimensional analysis cannot, therefore, be expected to hold generally.

This is confirmed by Figs. 1 and 2 where two formulations of the corresponding states principle, representative for the present stage of research, are investigated.

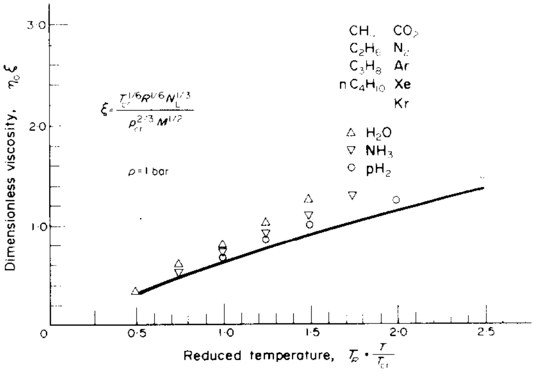

FIG. 1. Dimensionless viscosity of several dilute gases.

Figure 1 shows the dimensionless viscosity $\eta\xi$ of some dilute gases as a function of the reduced temperature T/T_{cr}. The parameter ξ is defined in the diagram, subscript cr denotes the critical point. The experimental values for all

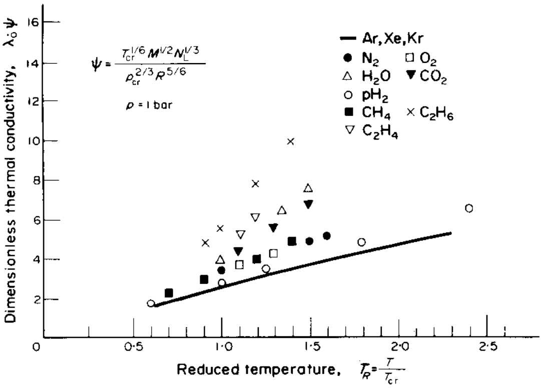

FIG. 2. Dimensionless thermal conductivity of several dilute gases.

investigated substances except water, ammonia and p-hydrogen fall on a single curve with a maximum deviation of ±4 per cent. They confirm the validity of the investigated formulation of the corresponding states principle even for substances which do not obey precisely the restrictions of the molecular model. The experimental values for water, ammonia and p-hydrogen clearly deviate from the general curve of the other fluids. For water and ammonia, this is commonly attributed to strong intermolecular polarity effects, whereas for p-hydrogen quantum effects are made responsible for the deviations. In the literature, many more fluids are known that deviate from the solid line in Fig. 1 [1–3].

Figure 2 shows the analogous investigation for the dimensionless thermal conductivity $\lambda\psi$ of some dilute gases. Only the noble gases without helium, which obey closely the restrictions of the molecular model, follow a common representation. They are shown by the solid line. The diatomic substances nitrogen and oxygen can also be correlated by a common curve which, however, differs from that of the noble gases. All the other substances deviate considerably from these two groups as well as among each other. They do not fit into the investigated formulation of the corresponding states principle. The large deviations are mainly attributed to the influence of internal degrees of freedom, which, contrary to viscosity, strongly affect the numerical value of thermal conductivity. The degree of accuracy to which these formulations of the corresponding states principle reproduce experimental values for gases at high pressures is of the same order of magnitude as for dilute gases. It is fair in the case of viscosity, if polar and quantum fluids as well as substances with long molecular chains are excluded. It is completely unsatisfactory for thermal conductivity, if fluids other than the noble gases are considered. For liquids, these correlations fail to give reasonable results.

Many efforts have been made to extend the regions of validity of such relations by introducing additional parameters. In the case of viscosity, the critical compressibility factor has been shown to improve the correlation for polar substances [3]. An additional quantum parameter has been shown to correlate the quantum fluids with the noble gases [4, 5]. For thermal conductivity, the specific heat capacity of a substance has proved useful as a parameter that takes into account the internal degrees of freedom of substance [6].

Such efforts, though valuable as an effective correlation technique, have not been able to overcome the fundamental limitation to groups of similar substances. The individual peculiarities of the fuids are too numerous to be taken into account by a limited number of empirical parameters. These additional parameters have thus merely extended the regions of validity of specific correlations from small groups to wider groups of substances.

It is suggested to denote all correlations with this limitation as classical formulations of the corresponding states principle.

3. A NEW CONCEPT

It is the purpose of this paper to develop new formulations of the corresponding states principle for transport properties which are not restricted to groups of similar fluids. The deduction of such universally valid correlations must not originate at the molecular structure of the substances. As has been indicated by the above considerations, this procedure necessarily leads to a practically unavoidable limitation to similar substances. A development of universal validity must start from characteristic phenomena of the transport properties which are common to all fluids. It is, therefore, only conceivable within the framework of phenomenological thermodynamics.

In the following considerations, the fundamental objective of the corresponding states principle, an universal relation of the transport property to the thermodynamic variables of state, will basically be assumed to exist. It will not, however, be postulated for a coherent region of states, but merely for discreet selected points on the surface representing all possible thermodynamic states in the (TP, T, p)-space. Here TP is the general symbol for a transport property. Such points represent true corresponding states, where all substances show a corresponding behavior if the considered properties are reduced with the coordinates of the considered point.

It is plausible to assume that such points—if they exist at all—should be distinguished universally, that is in the same way for all substances, on the described thermodynamic surface.

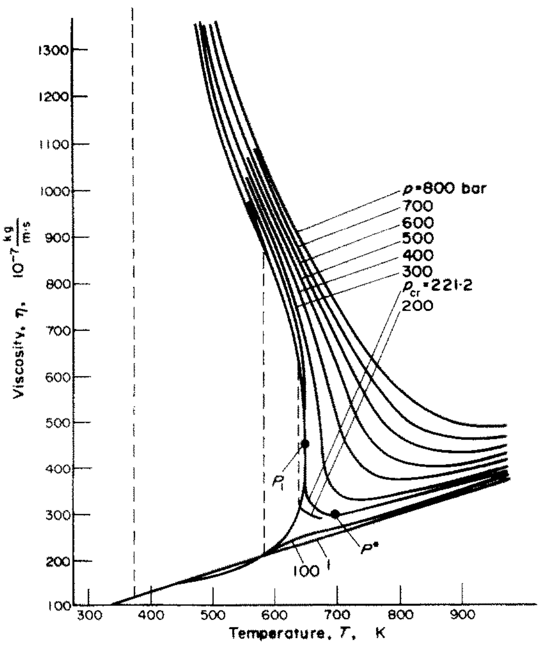

FIG. 3. (η-T-p)-diagram for water.

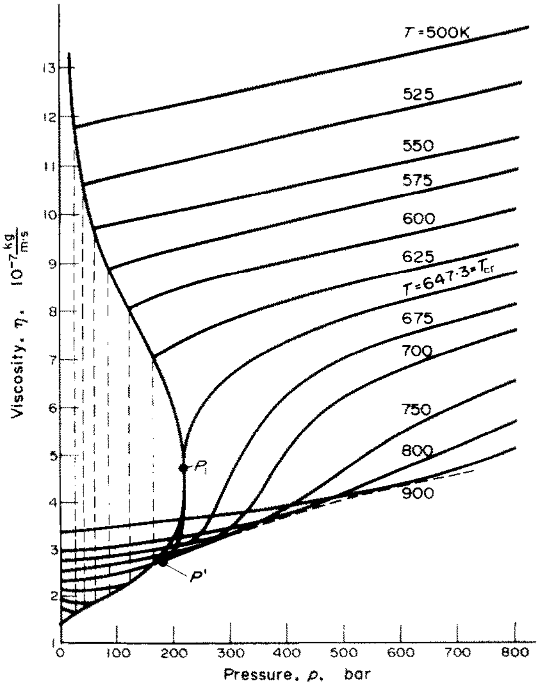

FIG. 4. (η-p-T)-diagram for water.

4. THE DISTINGUISHED REFERENCE POINTS

Starting from an investigation by Straub [7] about a new formulation of the corresponding states principle for (p-v-T)-data, the surfaces of viscosity and thermal conductivity were examined systematically for such universally distinguished points.

Figures 3 and 4 show two representations of the state diagram for water which may be considered typical for all pure substances. The points P1, P* and P′ are universally distinguished from all other points in the diagram. They are each defined by two independent thermodynamic relations which are the same for all fluids. These two relations determine the two independent variables temperature and pressure of the considered point.

Point P1 is defined in Fig. 3 by:

$$\left[\left(\frac{\partial T}{\partial \eta}\right)_p\right]_{\mathrm{P1}} = 0 \tag{3}$$

and

$$\left[\left(\frac{\partial^2 T}{\partial \eta^2}\right)_p\right]_{\mathrm{P1}} = 0. \tag{4}$$

By these two relations, P1 is universally determined on the (η-T-p) surface.

In Fig. 4, analogous relations hold for P1. It may be shown by rigorous thermodynamic arguments, that P1 is identical with the critical point, where the first two derivatives of pressure with respect to specific volume vanish at constant temperature.

Point P* in Fig. 3 is determined as the minimum of that isobar which is distinguished from all other lines of constant pressure by its vertical tangent at P1. This again gives two universal thermodynamic relations for the two independent variables T and p at this point.

The mathematical description is:

$$\left[\left(\frac{\partial \eta}{\partial T}\right)_p\right]_{\mathrm{P*}} = 0 \tag{5}$$

and

$$[p]_{\mathrm{P*}} = p^* = p_{\mathrm{cr}}. \tag{6}$$

The only isobar with a vertical tangent is the critical. P* thus is the minimum of the critical isobar.

Point P′ in Fig. 4 is seen to be the point of contact between the critical isotherm, which is distinguished by a vertical tangent, and the curve enveloping all isotherms. The mathemathematical representation is:

$$\left[\left(\frac{\partial f(\eta, p, T)}{\partial T}\right)_{\eta, p}\right]_{\mathrm{P'}} = 0 \tag{7}$$

as the condition for the envelope of the isotherms, and

$$[T]_{\mathrm{P'}} = T' = T_{\mathrm{cr}} \tag{8}$$

as the condition for the distinguished critical isotherm. It can be shown that P′ is the minimum of the isobar at the critical temperature.

In Figs. 5 and 6, two analogous representations of the thermal conductivity surface are shown, again for water. The curves are very similar to those for viscosity, resulting in analogous distinguished points P1, P* and P′. Point P2 in Fig. 5, the maximum of the critical isobar, does not appear to be a general phenomenon of all fluids. From the substances investigated, it was only verified for water and p-hydrogen. It will therefore not be considered further.

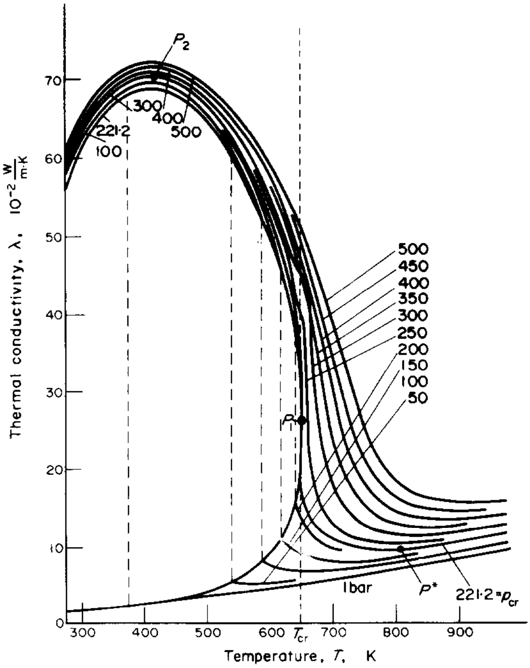

FIG. 5. (λ-T-p)-diagram for water.

5. FORMULATION OF THE THEORY

It shall be assumed that the isotherms through the considered distinguished points may be represented by a Taylor expansion in powers of pressure around $p = 0$.

For the transport property TP, this expansion may be written, if all variables are reduced with

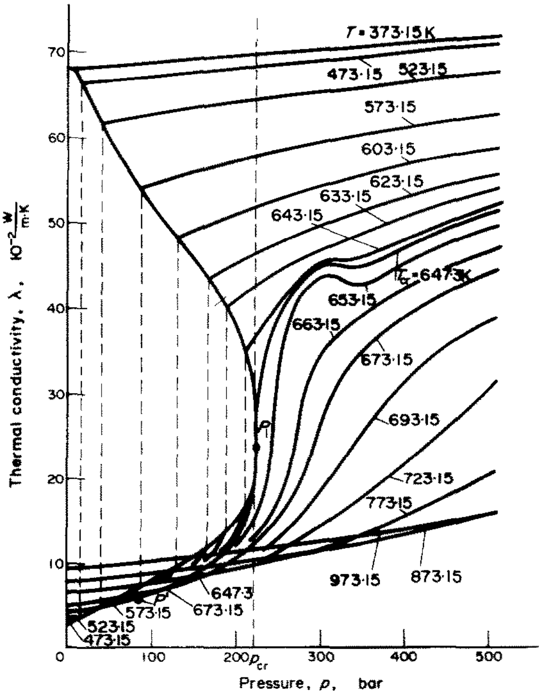

FIG. 6. (λ-p-T)-diagram for water.

the corresponding coordinates of the distinguished point:

$$\mathrm{TP}_R(T_R = 1, p_R) = \sum_{\nu=0}^{\infty} A_\nu p_R^\nu \tag{9}$$

where the index R denotes reduced quantities.

The coefficients A_ν of the Taylor expansion are defined as

$$A_0 = \frac{\mathrm{TP}(T_R = 1,\, p_R = 0)}{\mathrm{TP}(T_R = 1, p_R = 1)}$$

$$= \mathrm{TP}_R(T_R = 1, p_R = 0) \tag{10}$$

and

$$A_\nu = \frac{1}{\nu!}\left[\frac{\partial^\nu \mathrm{TP}_R(T_R = 1, p_R)}{\partial p_R^\nu}\right]_{p_R=0},$$

$$\nu = 1, 2, 3, \ldots. \tag{11}$$

Equation (9) represents the functional dependence of the reduced transport property on reduced pressure at the temperature of the considered point. This representation is universally valid for all substances, all variables being reduced to dimensionless form by universally defined quantities.

For the n-th derivation of the reduced transport property with respect to reduced pressure at the temperature of the distinguished point, one may write:

$$\left(\frac{\partial^n \mathrm{TP}_R}{\partial p_R^n}\right)_{T_R=1} = n!\sum_{\nu=n}^{\infty}\binom{\nu}{n}A_\nu p_R^{\nu-n}. \tag{12}$$

Assuming that this series still converges in the distinguished point the n-th derivation becomes at this point:

$$\left(\frac{\partial^n \mathrm{TP}_R}{\partial p_R^n}\right)_{\substack{T_R=1\\ p_R=1}} = \mathrm{TP}_{Rn} = n!\sum_{\nu=n}^{\infty}\binom{\nu}{n}A_\nu. \tag{13}$$

Equation (13) represents an infinite system of equations for the infinite number of coefficients A_ν, once the derivations of the left side are known.

The first line of this system, for $n = 0$, can be written as

$$1 = A_0 + A_1 + A_2 + A_3 + \ldots \tag{14}$$

In this equation, A_0 may be taken arbitrarily as the independent variable. It is then clear that at least one of the A_ν for $\nu \neq 0$, possibly all, should depend on A_0 in order to satisfy equation (14). From the universally valid system of equations (13) this results in the statement that all derivations at a distinguished point depend universally on A_0. Within the region of convergence of the universal Taylor expansion (9) the reduced transport property at $T_R = 1$ is thus a universal function of reduced pressure and A_0. This is the statement of the universal formulation of the corresponding states principle for the transport property TP.

The condition of convergence at the distinguished point eliminates point P1, i.e. the critical point, from further consideration. The critical isotherm has a vertical tangent there. Its Taylor expansion will, therefore, not converge at this point. Consequently at least one of the left sides in equation (13) will become infinite, if applied to P1 as reference point. Points on transport property surfaces that are universally distinguished in the sense discussed above and that satisfy the additional restrictions concerning the functional representation of the corresponding isotherms will be termed points of correspondence.

6. COMPARISON WITH EXPERIMENTAL VALUES

In Tables 1 and 2, the coordinates of the points P* and P′ have been compiled for the viscosity of the substances investigated. The ratio T^*/T_{cr} resp. p'/p_{cr} has been included as a criterion for the deviation from the classical reference state, the critical point. The last row contains literature resources for experimental values. The corresponding informations for thermal conductivity are shown in Tables 3 and 4. The coefficient A_0, defined by equation (10), may be easily evaluated from experimental transport property values. It is found that the dependence on the substance, if any, is negligibly small, A_0 having approximately the same value for all substances investigated.

Figures 7 and 8 show this for measurements of viscosity for the points P* and P′ respectively. All experimental points fall indeed on a universal straight line with only small scattering. In Fig. 7, the average deviation is 1·3 per cent, the maximum deviation 4·0 per cent for xenon.

Table 1. Coordinates of point P for the viscosity of several substances*

Substance	p^* (bar)	T^* (K)	η^* (10^{-7} kg/ms)	T^*/T_{cr} —	Ref.
Ar	48·6	173	166	1·14	[8–10]
Xe	58·4	330	311	1·14	[9, 11, 12]
pH_2	12·8	38	23	1·15	[13]
N_2	34·0	143	117	1·13	[9, 14–16
CH_4	46·2	214	96	1·12	[17–19]
C_2H_6	49·2	348	129	1·14	[18, 20, 21]
C_3H_8	42·5	421	134	1·14	[18, 21, 22]
nC_4H_{10}	38·0	476	138	1·12	[18, 23, 24]
iC_4H_{10}	36·4	463	131	1·13	[21, 25]
nC_5H_{12}	33·8	535	148	1·14	[26–28]
C_2H_4	50·6	322	131	1·14	[29]
CO_2	73·7	341	197	1·12	[30–32]
NH_3	114·0	444	175	1·09	[33, 34]
H_2O	221·2	693	297	1·07	[35, 36]

Table 2. Coordinates of point P′ for the viscosity of several substances

Substance	p' (bar)	T' (K)	η' (10^{-7} kg/ms)	p'/p_{cr} —	Ref.
pH_2	9·3	33·0	290	0·72	[13]
CH_4	30·6	190·7	86	0·66	[17–19]
C_2H_6	32·0	305·4	112	0·65	[18, 20, 21]
C_3H_8	32·8	369·9	122	0·77	[18, 21, 22]
CO_2	61·4	304·2	183	0·83	[30–32]
NH_3	97·0	405·5	164	0·85	[33, 34]
H_2O	185·0	647·4	275	0·85	[35, 36]

Table 3. Coordinates of point P for the thermal conductivity of several substances*

Substance	p^* (bar)	T^* (K)	λ^* 10^{-2} W/mK	T^*/T_{cr} —	Ref.
Ar	48·6	190	1·63	1·26	[37]
N_2	33·5	153	1·92	1·21	[38]
O_2	50·7	189	2·25	1·22	[39]
pH_2	12·8	403	3·96	1·22	[40]
CH_4	46·2	224	3·15	1·18	[41]
C_2H_6	48·2	335	3·39	1·10	[42]
CO_2	73·7	366	2·80	1·20	[43]
N_2O	72·6	356	2·77	1·16	[44]
NH_3	114·0	500	6·50	1·23	[45]
H_2O	221·2	810	9·70	1·25	[35]

Table 4. Coordinates of point P′ for the thermal conductivity of several substances

Substance	p' (bar)	T' (K)	λ' 10^{-2} W/mK	p'/p_{cr} —	Ref.
pH_2	8·1	33·0	3·20	0·63	[37]
CH_4	27·8	190·7	2·60	0·60	[41]
C_2H_6	32·4	305·4	2·80	0·66	[42]
CO_2	42·7	304·2	2·20	0·58	[43]
N_2O	46·5	309·7	2·30	0·64	[44]
NH_3	45·5	405·5	4·80	0·40	[45]
H_2O	76·0	647·4	6·55	0·35	[35]

In Fig. 8, for P′ as reference state, the corresponding deviations are 1·8 per cent and 4·6 per cent for methane. The polar substances water and ammonia as well as the quantum fluid p-hydrogen have lost their exceptional position.

Figures 9 and 10 show the analogous representations for thermal conductivity. Here again the experimental values for all fluids fall on one straight line, thus demonstrating the universality of A_0. The average deviations for the reference points P* and P′ are 1·7 per cent and 0·3 per cent, the maximum deviations 3·8 for water and 0·7 per cent for carbon dioxide respectively.

As a result of equations (13) and (14) this

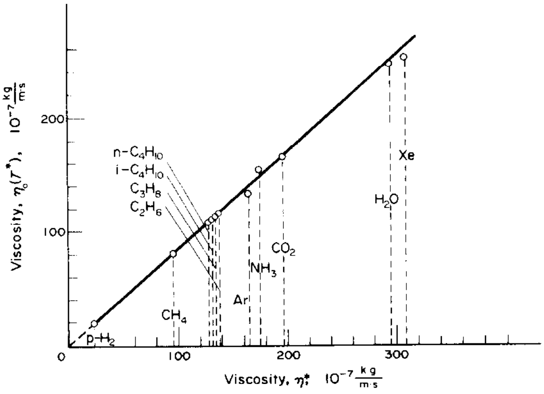

FIG. 7. Universality of A_0 for viscosity and P* as point of correspondence.

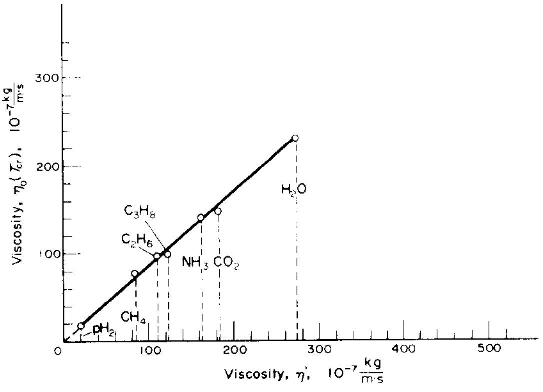

FIG. 8. Universality of A_0 for viscosity and P′ as point of correspondence.

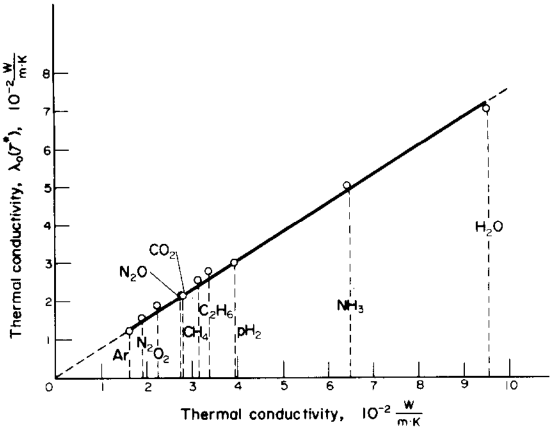

FIG. 9. Universality of A_0 for thermal conductivity and P* as point of correspondence.

implies universality for the remaining Taylor expansion coefficients $A_v(v = 1, 2, 3 \ldots)$. A plot of the reduced transport property against reduced pressure at the temperature of a distinguished point must therefore be universal for all substances within the region of convergence of equation (9). This is the specific statement of the new formulation of the corresponding states principle for viscosity and thermal conductivity with P^* and P' as reference points. Only point P* has been investigated in this representation, as values for the critical isotherm, that is T', could not be obtained with sufficient accuracy for a reasonable number of substances.

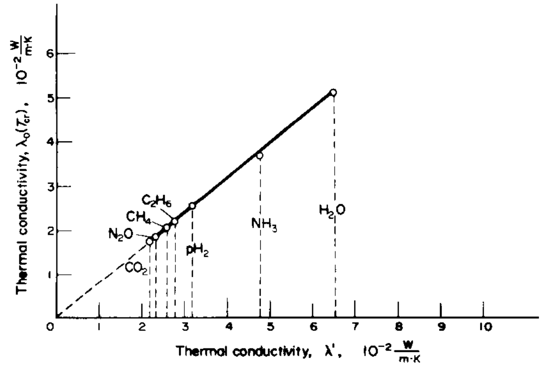

FIG. 10. Universality of A_0 for thermal conductivity and P′ as point of correspondence.

Figure 11 shows this plot for the viscosity of the investigated substances. Up to a reduced pressure of $p/p^* = 2{\cdot}2$, all experimental points coincide on one universal curve thus confirming the universality of the coefficients A_v. For pressures higher than $p/p^* = 2{\cdot}2$, the experimental values for water and p-hydrogen deviate increasingly from the universal curve of the other fluids. These deviations are too large and too systematic to be caused by experimental errors. The reason for this phenomenon may rather be attributed to the fact that this plot is only relevant within the region of convergence of equation (9). For pressures beyond this region, the universality of the Taylor expansion coefficients does not imply a universal representation of the reduced transport property according to Fig. 11. This plot is then no more than one of the many possible classical formulations of the corresponding states principle,

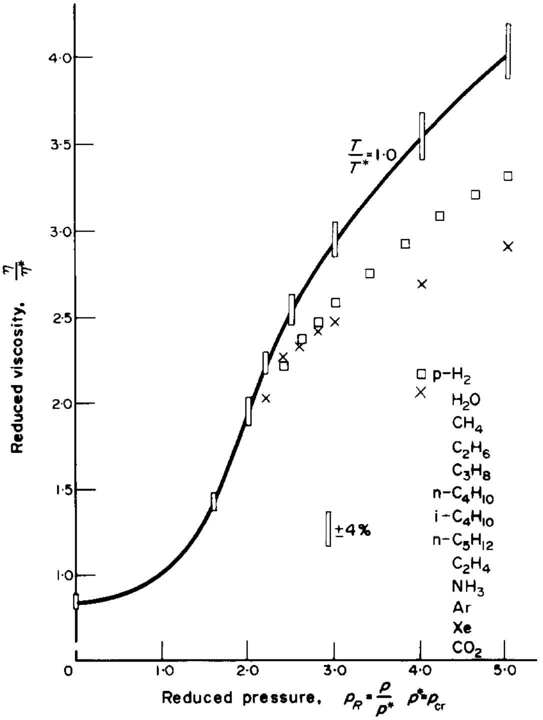

FIG. 11. Universal representation of reduced viscosity as a function of reduced pressure for P* as point of correspondence.

which, as has been discussed before, are not able to correlate highly polar and quantum substances. The deviations of water and p-hydrogen in Fig. 11 thus indicate a limit of the convergence region for equation (9) at $p/p^* = 2{\cdot}2$. They do not, however, question the validity of the universal formulation of the corresponding states principle for viscosity.

Figure 12 shows the analogous plot for thermal conductivity. Up to pressures $p/p^* = 3{\cdot}0$, the reduced thermal conductivity is a universal function of reduced pressure at the temperature T^* within experimental error. At $p/p^* = 4{\cdot}0$, the deviations of p-hydrogen (6·0 per cent) and ethane (10 per cent) appear to indicate that the region of convergence of equation (9) has been exceeded. The final decision on this phenomenon will have to be postponed until reliable measurements for more substances become available at this pressure.

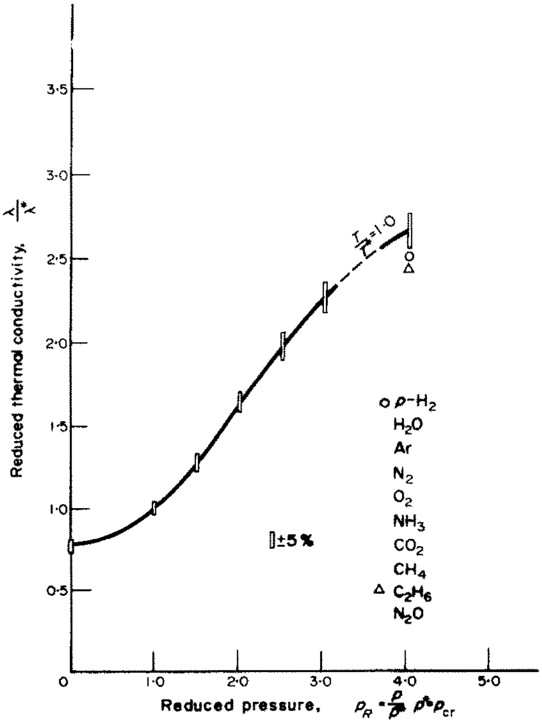

FIG. 12. Universal representation of reduced thermal conductivity as a function of reduced pressure for P* as point of correspondence.

The theoretical results for viscosity and thermal conductivity may thus be considered to be adequately confirmed.

It appears justified now to generalize the results, confirmed for a limited number of substances, for all fluids with only two independent variables, temperature and pressure. These two variables are unambiguously and universally defined in each point of correspondence by two thermodynamic relations. The universal validity cannot be proved rigorously by phenomenological arguments. The investigated substances have, however, very different molecular structures and have so far resisted all efforts of being forced into a generalized representation. According to the usual approach in phenomenological thermodynamics, one may therefore accept the described universal behavior in distinguished points to be valid for all substances as long as it is not falsified in any case by experimental observation.

7. PRACTICAL APPLICATION

The universal representation of a reduced transport property as a function of reduced pressure is restricted to a single temperature, the isotherm through a point of correspondence. For practical application, one cannot be satisfied with an information about one or two temperatures alone. Methods have to be found, therefore, to extrapolate from one universal isotherm to a wide region of states.

For this purpose, the results of Fig. 11 and 12 shall be presented in the following form:

$$\frac{\mathrm{TP}(T^*/T^*, p/p^*)}{\mathrm{TP}^*} - A_0^* = f_u^p(p/p^*). \qquad (15)$$

A_0^* is a universal constant and $f_u^p(p/p^*)$ a universal function which are known from reliable measurements of one single substance, for instance water.

Using p-v-T-data or an equation of state, the pressure function in equation (15) at the temperature T^* can be transformed into a density function, to give

$$\frac{\mathrm{TP}(T^*/T^*, \rho/\rho^*)}{\mathrm{TP}^*} - A_0^* = f^\rho(\rho/\rho^*). \quad (16)$$

The density function $f^\rho(\rho/\rho^*)$ contains an individual equation of state and will therefore be specific for each substance. If the definition of A_0^*, equation (10), is introduced, one receives from equation (16):

$$\frac{\mathrm{TP}(T^*/T^*, \rho/\rho^*)}{\mathrm{TP}^*} - \frac{\mathrm{TP}_0(T^*/T^*)}{\mathrm{TP}^*} = f^\rho(\rho/\rho^*). \quad (17)$$

Equation (17) is identical to the residual transport property concept according to which the isothermal difference between two values of the transport property at high density and in the dilute gas limit is a function of density alone and is independent of temperature. The density function $f^\rho(\rho/\rho^*)$ thus takes into account the isothermal increase of the transport property with density at any temperature, not only at T^*. This phenomenon has been verified in the case of viscosity and thermal conductivity for practically all substances for which experimental values exist [46, 47].

For viscosity, the residual concept may be considered to hold for densities up to twice the critical and temperatures up to ten times the critical. For higher densities, increasing deviations are observed the lower the temperature, that is especially in the high pressure liquid region [46]. As an exception, deviations up to 10 per cent have been found for p-hydrogen in the total region of states [13].

For thermal conductivity, the residual correlation fails in the vicinity of the critical point. The states between 0·9 times and 1·2 times the critical temperature from 0·5 times to 1·5 times the critical density have to be excluded from the correlation. Apart from this critical region and very high liquid densities, the residual concept for thermal conductivity holds with fair accuracy [47, 48].

Using the residual concept, the numerical value of a transport property for a given thermodynamic state (T, ρ) can be calculated from the following expression:

$$\frac{\mathrm{TP}(T/T^*, \rho/\rho^*)}{\mathrm{TP}^*} = \frac{\mathrm{TP}_0(T/T^*)}{\mathrm{TP}^*} + f^\rho(\rho/\rho^*). \quad (18)$$

Here the fact has been used that the density function $f^0(\rho/\rho^*)$ describes the increase of the transport property with density at any temperature T. The values for TP* and p^* are given from the coordinates of the point of correspondence P^*. The function $f^\rho(\rho/\rho^*)$ as well ρ^* is known from the universal pressure function $f_u(p/p^*)$ and the equation of state. As an additional information, the value of the transport property in the dilute gas limit TP_0 is needed.

8. CONCLUDING REMARKS

The fundamental objective of the corresponding states principle as applied to transport properties is the universal representation of their temperature and pressure dependence. In this investigation, this objective has been confined and specified to distinguished, universally defined points on the transport property surface. A number of substances with rather different molecular properties has thus been described by a new formulation of the corresponding states principle. This formulation does not originate at molecular structure and does, therefore, not depend on it. The investigated substances are considered representative for the total number of those fluids, for which viscosity and thermal conductivity depend on two variables, temperature and pressure, alone. In this respect, the suggested formulations of the corresponding states principle may be termed universal. Non-Newtonian substances thus have to be excluded from the consideration.

Numerical values for the transport properties of pure dense fluids can be calculated from these universal formulations of the corresponding states principle, if the point of correspondence, the equation of state and the transport property in the dilute gas limit are known. A problem which is difficult experimentally and still unsolved theoretically has thus been reduced to determining the transport property of the dilute gas and the equation of state, provided that the point of correspondence is known. These two tasks have either been solved theoretically to a large extent or at least can be mastered much easier by experiments.

ACKNOWLEDGEMENTS

The author is indebted to Prof. K. Stephan, Dr. A.Schaber and Dr. D. Straub for many helpful discussions. The work was supported financially by the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen, Federal Republic of Germany, which is gratefully acknowledged.

REFERENCES

1. K. Lucas, Die Berechnung der Transportgrössen reiner fluider Stoffe nach dem Korrespondenzprinzip. Diss. T.U. Berlin, D 83 (1971).
2. R. C. Reid and T. K. Sherwood, *The Proporties of Gases and Liquids*. McGraw-Hill, New York (1966).
3. L. I. Stiel and G. Thodos, Viscosity of polar gases at normal pressures, *A.I.Ch. E. Jl* **8**, 229–232 (1962).
4. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*. John Wiley, New York (1964).
5. J. F. Kerrisk, J. D. Rogers and E. F. Hammel, Transport properties of He^3, He^4, H_2, D_2, T_2 and Ne in the liquid state according to the quantum mechanical principle of corresponding states, *Adv. Cryogen. Engng* **9**, 188–196 (1964).
6. D. Misic and G. Thodos, The thermal conductivity of hydrocarbon gases at normal pressures, *A.I. Ch. E. Jl* 7, 264–267 (1961).
7. D. Straub, Zur Theorie eines allgemeinen Korrespondenzprinzips der thermischen Eigenschafter fluider Stoffe, Diss. Karlsruhe (1964).
8. A. G. Clarke and E. B. Smith, Viscosities of Ar, Kr and Xe, *J. Chem. Phys.* **48**, 3988–3994 (1968).
9. J. A. Gracki, G. P. Flynn and J. Ross, Viscosity of N_2, H_2, He and Ar, *J. Chem. Phys.* **51**, 3856–3863 (1969).
10. A. Michels, A. Botzen and W. Schuurman, The viscosity of Ar at pressures up to 2000 atm, *Physica* **20**, 1144–1156 (1954).
11. M. Rigby and E. B. Smith, Viscosities of the inert gases, *Trans. Farad. Soc.* **62**, 55–57 (1966).
12. N. J. Trappeniers, A. Botzen, H. R. van den Berg and J. van Oosten, The viscosity of Ne between 25 and 75°C at pressures up to 1800 atm, *Physica* **30**, 985–996 (1964).
13. D. E. Diller, Measurements of the viscosity of pH_2, *J. Chem. Phys.* **42**, 2089–2100 (1965).
14. A. G. Clarke and E. B. Smith, Low-temperature viscosities and intermolecular forces of simple gases, *J. Chem. Phys.* **51**, 4156–4166 (1969).
15. J. T. F. Kao and R. Kobayashi, Viscosity of He and N_2 and their mixtures at low temperatures and elevated pressures, *J. Chem. Phys.* **47**, 2836–2849 (1967).
16. K. Goldman, Viscosity of N_2 at low temperatures and high pressures, *Physica* **29**, 510–515 (1963).
17. E. T. S. Huand, G. W. Swift and F. Kurata, Viscosity of $CH_4C_3H_8$ at low temperatures and high pressures, *A.I.Ch. E. Jl* **12**, 932–936 (1966).
18. D. Ans-Lax, *Taschenbuch für Chemiker und Physiker*, Bd. 1. Springer, Berlin (1967).
19. L. T. Carmichael, V. Berry and B. H. Sage, Viscosity at high pressure, *J. Chem. Engng Data* **8**, 94–98 (1963).
20. L. T. Carmichael and B. H. Sage, Viscosity of C_2H_6 at high pressure, *J. Chem. Engng Data* **8**, 94–98 (1963).
21. *API-Technical Data Book*, chap 11, *Viscosity*. American Petrol Institute (1964).
22. L. T. Carmichael, V. M. Berry and B. H. Sage, Viscosity of hydrocarbons—propane, *J. Chem. Engng Data* **9**, 411–415 (1964).
23. L. T. Carmichael and B. H. Sage, Viscosity of hydrocarbons—n-butane, *J. Chem. Engng Data* **8**, 612–616 (1963).
24. J. P. Dolan, K. E. Starling, A. L. Lee and B. E. Eakin, Liquid gas and dense fluid viscosity of n-Butane, *J. Chem. Engng Data* **8**, 396–399 (1963).
25. M. H. Gonzales and A. L. Lee, Viscosity of isobutane, *J. Chem. Engng Data* **11** (1966), 357–359.
26. J. C. McCoubrey and N. M. Singh, The vapor phase viscosities of the pentanes, *J. Chem. Phys.* **67** 517–518 (1963).
27. N. A. Agayev and I. F. Golubev, Viscosity of pentane and hexane, *Gaz. Prom.* **8** 45–50 (1963).
28. A. L. Lee and R. T. Ellington, Viscosity of n-pentane *J. Chem. Engng Data* **10**, 101–104 (1965).
29. E. W. Comings, B. J. Mayland and R. S. Egly, The viscosity of gases at high pressures, *Univ. Ill. Bull.* **42** (1944).
30. R. Dipippo and J. Kestin, Viscosity of seven gases up to 500°C and its statistical interpretation, proc. 4th symp. thermophysical prop. ASME, 304–313 (1968).
31. A. Michèls, A. Botzen and W. Schuurman, The viscosity of CO_2 between 0°C and 75°C at pressures up to 2000 atm, *Physica* **23**, 95–102 (1957).
32. J. Kestin, J. H. Whitelaw and T. F. Zien, The viscosity of CO_2 in the neighbourhood of the critical point, *Physica* **30**, 161–181 (1964).
33. L. G. Burch and C. J. G. Row, Viscosities of ammonia–methylamine mixtures, *J. Chem. Phys.* **47**, 2798–2801 (1967).
34. L. T. Carmichael, H. H. Reamer and B. H. Sage, Viscosity of ammonia at high pressures, *J. Chem. Engng Data* **8** 400–404 (1963).
35. U. Grigull, F. Mayinger and J. Bach, Viscosität, Wärmeleitfähigkeit und Prandtl-Zahl von Wasser und Wasserdampf, *Wärme- und Stoffübertragung* **1**, 15–34 (1968).
36. K. H. Dudziak and E. U. Franck, Messungen der Viskosität des Wassers bis 560°C und 3500 bar, *Berichte der Bunsengesellschaft* **70**, 1120–1128 (1966).
37. J. Bailey and K. Kellner, The thermal conductivity of liquid and gaseous Ar, *Physica* **39**, 444–462 (1968).

38. H. Ziebland and J. T. A. Burton, The thermal conductivity of N_2 and Ar in the liquid and gaseous states, *Br. J. Appl. Phys.* **9**, 52–59 (1958).
39. H. Ziebland and J. T. A. Burton, The thermal conductivity of liquid and gaseous oxygen, *Br. J. Appl. Phys.* **6**, 416–420 (1955).
40. H. M. Roder and D. E. Diller, Thermal conductivity of gaseous and liquid hydrogen, *J. Chem. Phys.* **52**, 5928–5949 (1970).
41. L. D. Ikenberry and S. A. Rice, On the kinetic theory of dense fluids XIV, *J. Chem. Phys.* **39**, 1561–1571 (1963).
42. L. T. Carmichael, V. Berry and B. H. Sage, Thermal conductivity of fluids, ethane, *J. Chem. Engng Data* **8**, 281–285 (1963).
43. A. Michels, J. V. Sengers and P. S. van der Galik, The thermal conductivity of CO_2 in the critical region, *Physica* **28**, 1216–1237 (1962).
44. G. N. Richter and B. H. Sage, Thermal conductivity of fluids N_2O, *J. Chem. Engng Data* **8**, 221–225 (1963).
45. D. P. Needham and H. Ziebland, The thermal conductivity of liquid and gaseous NH_3 and it anomalous behavior in the vicinity of the critical point. *Int. J. Heat Mass Transfer* **8**, 1387–1414 (1965).
46. K. Lucas, Die Viskosität reiner Flüssigkeiten in der Nähe der kritischen Temperatur, *Wärme- und Stoffübertragung* **4**, 4 (1971).
47. D. E. Diller, H. J. M. Hanley and H. M. Roder, The density and temperature dependence of the viscosity and thermal conductivity of dense simple fluids, *Cryogenics*, August, 286–294 (1970).
48. L. T. Stiel and G. Thodos, The thermal conductivity of non-polar substances in the dense gaseous and liquid regions, *A.I.Ch. E. Jl* **10**, 2630 (1964).

NOUVELLES FORMULATIONS DU PRINCIPE DES ETATS CORRESPONDANTS POUR LES PROPRIETES DE TRANSPORT DE FLUIDES PURS ET DENSES

Résumé—Les formulations usuelles du principe des états correspondants sont réduites aux groupes de substances similaires. Ceci peut être justifié par leur base théorique commune qui est un modèle de gaz moléculaire très idéalisé. Dans cet article, une nouvelle approche du développement des formulations du principe des états correspondants sans cette limitation est présentée pour les propriétés de transport de fluides purs et denses, viscosité et conductivité thermique. La théorie est basée sur le concept d'un point de correspondance qui est un point universellement considéré sur la surface à propriétés de transport à partir de laquelle un comportement universel des propriétés de transport est postulé et rendu plausible pour tous les fluides. Sur cette base, la propriété réduite de transport à la température du point de correspondance devient une fonction universelle de la pression réduite. Ce résultat théorique est vérifié pour plusieurs fluides qui n'auraient pas pu être introduits antérieurement dans une formulation commune. Le résultat universel pour une isotherme est généralisé par utilisation du concept résiduel pour les propriétés de transport.

NEUE FORMULIERUNGEN DES KORRESPONDENZPRINZIPS FÜR DIE TRANSPORTKOEFFIZIENTEN REINER DICHTER FLUIDE

Zusammenfassung—Die bekannten Formulierungen des Korrespondenzprinzips sind lediglich für Gruppen aus ähnlichen Stoffen gültig. Diese Einschränkung ergibt sich aus dem allen diesen Korrelationen als gemeinsame theoretische Basis zugrundeliegenden, idealisierten Molekülmodell. In dieser Arbeit wird eine neue Methode zur Herleitung von Formulierungen des Korrespondenzprinzips ohne diese Einschränkung angegeben, und zwar für die Transportkoeffizienten reiner, dichter Fluide, Viskosität und Wärmeleitfähigkeit. Die Theorie basiert auf dem Konzept eines Korrespondenzpunktes, d.h. einem universell ausgezeichneten Punkt auf der Zustandsfläche der Transportgröße, an dem ein universelles Verhalten der Transportgrößen für alle Stoffe nachgewiesen wird. Auf dieser Basis wird die normierte Transportgrösse bei der Temperatur des Korrespondenzpunktes eine universelle Funktion des Druckes. Dieses theoretische Ergebnis wird für eine Reihe von Stoffen verifiziert, die sich bisher allen Bemühungen um eine gemeinsame Darstallung entzogen haben. Das universelle Resultat für eine Isotherme wird mit Hilfe des Restgrößenkonzeptes für die Transport koeffizienten verallgemeinert.

НОВАЯ ФОРМУЛИРОВКА ЗАКОНА СООТВЕТСТВЕННЫХ СОСТОЯНИЙ ДЛЯ СВОЙСТВ ПЕРЕНОСА ЧИСТЫХ ПЛОТНЫХ ГАЗОВ

Аннотация—Обычная формулировка закона соответственных состояний применяется только к группам подобных веществ, что связано с теоретически допускаемой идеализированной моделью молекулы газа. В данной работе применен новый подход к формулировке закона соответственных состояний для свойств переноса чистых плотных газов (вязкости и теплопроводности), который свободен от такого ограничения. Теория основана на понятии о точке соответствия, т.е. об универсально выбранной точке на поверхности свойства переноса, в которой постулируется одинаковое поведение свойств переноса для всех газов. На этой основе приведенное свойство переноса при температуре точки соответствия становится универсальной функцией приведенного давления. Этот теоретический результат проверялся на нескольких газах, для которых ранее не удавалось получить обычной корреляции. Результаты одной изотермы обобщены для свойств переноса.