

EXTREMES IN DEPENDENCES OF ENTHALPY AND ENTROPY OF SATURATED VAPOUR ON TEMPERATUREJosef P. NOVAK^{a1}, Anatol MALIJEVSKY^{a2}, Jaroslav DEDEK^b and Jiri OLDRICH^c^a Department of Physical Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail: ¹ josef.novak@vscht.cz, ² anatol.malijevsky@vscht.cz^b Plynoprojekt Praha, 120 00 Prague 2, Czech Republic; e-mail: pnppraha@mbox.vol.cz^c CKD Kompresory a.s., 190 02 Prague 9, Czech Republic

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It was proved that the enthalpy of saturated vapour as a function of temperature has a maximum for all substances. The dependence of the entropy of saturated vapour on temperature can be monotonous, has a minimum and a maximum, or has only a maximum. The thermodynamic relations were derived for the existence of the extremes which enable their computation from the knowledge of dependence of the ideal-gas heat capacity on temperature and an equation of state. A method based on the theorem of corresponding states was proposed for estimating the extremes, and its results were compared with literature data. The agreement between the literature and estimated temperatures corresponding to the extremes is very good. The procedure proposed can serve for giving precision to the H - p and T - S diagrams commonly used in applied thermodynamics.

Key words: Enthalpy; Entropy; Saturated vapour.

The curve of saturated vapour, *i.e.*, the line separating the gas region from the liquid-vapour region, plays a significant role in the theoretical and applied thermodynamics. If a gas on compressing (at subcritical temperature) or on cooling crosses this boundary, a dramatic change takes place in the system – the liquid phase will appear in addition to the gas phase. This phenomenon is often undesirable. Let us consider an isentropic (*i.e.* reversible adiabatic) or isoenthalpic (*i.e.*, Joule–Thomson process) compression or expansion of the gas. Provided the curve of saturated vapour were crossed during these processes, a partial condensation of vapour would occur. In this way the density of medium would be considerably increased, which might result in a compressor breakdown. For these reasons the dependences are often studied of enthalpy of saturated vapour on pressure (*i.e.* on saturated vapour pressure) and the dependences of entropy of saturated vapour on condensation temperature; see, *e.g.*, refs^{1–3}.

It was observed that the enthalpy of saturated vapour as a function of saturated vapour pressure shows a maximum. The entropy of saturated vapour as a function of temperature may have a minimum and a maximum. It is possible to ask a question whether these extremes are typical of some or all the gases. Further we can ask what

thermodynamic data are needed to localize the extremes. As far as it is known to the authors, no attention has been paid to these questions in the open literature. The aim of this work is to answer them, to derive rigorous thermodynamic relations for the position of the extremes and to propose a method for estimating these positions.

THEORETICAL

Maximum in the Dependence of Saturated Vapour

The dependence of molar enthalpy H_m on pressure p (H - p diagram) is illustrated schematically in Fig. 1 at supercritical (T_4), critical (T_3), and two subcritical temperatures ($T_2, T_1, T_2 > T_1$). Line GCL separating the homogeneous region of fluid (liquid or gas) from the heterogeneous region in which coexist the gas and the liquid phases is depicted in the figure as well. This line consists of two branches – of branch GC, of the dependence of molar enthalpy of saturated vapour on the saturated vapour pressure and of branch CL, of the dependence of molar enthalpy of saturated liquid on the saturated vapour pressure. Symbol C denotes the critical point.

In this work we shall discuss the branch GC. One can observe the maximum E on it which divides this branch into two parts GE and EC. If we stem from the points lying

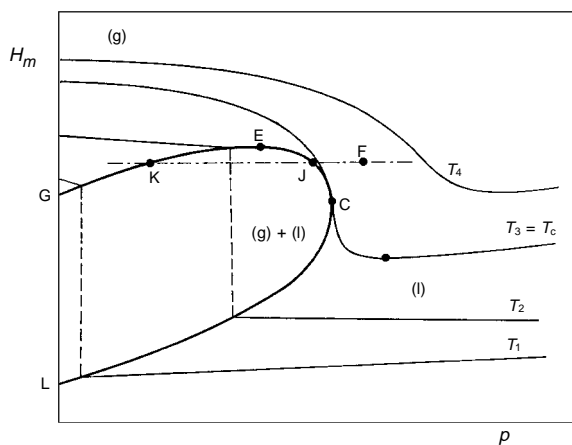


FIG. 1

Schematic sketch of the $H_m = H_m(p)$ diagram. Symbol (g) denotes the gas region, symbol (l) the liquid region. Solid line without designation separates the region of homogeneous fluid from the two-phase region, (g) + (l). C is the critical point. Solid lines with designation T_i are isotherms, the shape of isotherms in the two-phase region is denoted by dash line. E is the maximum in the dependence of enthalpy of saturated vapour on saturated vapour pressure. The meaning of points G, K, J, L, and F is explained in the main text. Dot-and-dash line designates isoenthalpic expansion (see main text)

on the curve GE, for instance from the point K, we shall get by isoenthalpic expansion always into the homogeneous gas phase. If we stem from the points lying on the curve EC, for instance from the point J, we may get by isoenthalpic expansion into the two-phase region. Into the two-phase region, we can get not only by isoenthalpic expansion of saturated vapour but also by expansion of fluid from the homogeneous region (for instance from the point F in the figure). It occurs in the cases when molar enthalpy is lower than the molar enthalpy at the maximum E, the initial pressure of expanding fluid is higher than the saturated vapor pressure and the pressure after the expansion is lower than saturated vapour pressure. The fact that during the isoenthalpic pressure drop (throttling), the condensation of gas takes place in the above-mentioned cases, may have serious technological consequences. It is therefore evident that the precise localization of the maximum E is important.

The maximum is determined by the condition

$$\left(\frac{dH_m}{dp}\right)_\sigma^{(g)} = 0, \quad (1)$$

where the subscript σ and superscript (g) denote that the derivative along the saturation curve and the saturated vapour are concerned, respectively. The molar enthalpy of pure substance is a function of two variables, temperature T and pressure p , $H_m = H_m(T, p)$. Along the saturation curve, pressure is equal to the saturated vapour pressure, $p = p^\theta$, which is an increasing function of temperature, $p^\theta = p^\theta(T)$, and it holds $H_m = H_m[T, p^\theta(T)]$. The condition for extreme (1) is therefore equivalent to the condition

$$\left(\frac{dH_m}{dT}\right)_\sigma^{(g)} = 0, \quad (2)$$

which can be written in the form

$$\left(\frac{dH_m}{dT}\right)_\sigma^{(g)} = \left(\frac{dH_m}{dT}\right)_p^{(g)} + \left(\frac{\partial H_m}{\partial p}\right)_T^{(g)} \left(\frac{dp^\theta}{dT}\right)_\sigma^{(g)} = C_{pm}^{(g)} + \left(\frac{\partial H_m}{\partial p}\right)_T^{(g)} \left(\frac{dp^\theta}{dT}\right)_\sigma^{(g)} = 0, \quad (3)$$

where $C_{pm}^{(g)}$ is the isobaric molar heat capacity of gas.

It is advantageous to divide $C_{pm}^{(g)}$ into two parts:

$$C_{pm}^{(g)}(T, p) = C_{pm}^0(T) + C_{pd}^{(g)}(T, p), \quad (4)$$

where C_{pm}^0 is the ideal-gas molar isobaric heat capacity and $C_{pd}^{(g)}$ is the correction for non-ideal behaviour of molar isobaric heat capacity (or also molar departure heat capacity⁴). We shall denote by ϕ_H the expression

$$\phi_H = -C_{pd}^{(g)} - \left(\frac{\partial H_m}{\partial p} \right)_T^{(g)} \left(\frac{dp^\sigma}{dT} \right)_\sigma \quad (5)$$

and the condition (1) for the extreme will be rewritten into the equivalent form

$$C_{pm}^0(T) = \phi_H(T) \quad (6)$$

The ideal-gas molar heat capacity C_{pm}^0 is always positive and finite. Let us investigate the course of function $\phi_H(T)$. For an ideal gas we have: $C_{pd}^{(g)} = 0$ and $(\partial H_m / \partial p)_T^{(g)} = 0$. With regard to Eq. (5), for an ideal gas also $\phi_H(T) = 0$. In the vicinity of the triple point, vapour behaves nearly as ideal gas because its saturated vapour pressure is here low. Therefore, $\phi_H(T)$ is small and

$$C_{pm}^0(T) > \phi_H(T) \quad (7)$$

At the critical point (the point C in Fig. 1),

$$\lim_{p \rightarrow p_c} \left(\frac{dH_m}{dp} \right)_\sigma^{(g)} = -\infty, \quad (8)$$

holds, where p_c is the critical pressure. It follows from that

$$\lim_{T \rightarrow T_c} \phi_H(T) = \infty, \quad (9)$$

where T_c is the critical temperature. Since $C_{pm}^0(T)$ is finite at all temperatures, in the vicinity of the critical point holds

$$C_{pm}^0(T) < \phi_H(T) \quad (10)$$

$\phi_H(T)$ is a continuous function of temperature. From inequalities (7) and (10) then follows that a temperature exists between the triple and critical points at which Eq. (6) will be fulfilled and that, at this temperature, the enthalpy of saturated vapour will have a maximum.

Extremes in the Dependence of Entropy of Saturated Vapour on Temperature

The dependence of molar entropy S_m on temperature is illustrated schematically in Fig. 2 at supercritical (p_4), critical (p_3) and two subcritical pressures (p_1 and p_2 , $p_2 > p_1$). Line GCL separates the homogeneous region of fluid (liquid or gas) from the heterogeneous region in which the gas and liquid phases coexist. This line consists of two branches – of branch GC, the dependence of entropy of saturated gas on boiling temperature, and branch CL, the dependence of entropy of saturated liquid on boiling temperature. The critical point is denoted by the symbol C. Let us remark that in the same way as it is common in technical practice, entropy is on the abscissa and temperature on the ordinate (T – S diagram) even though in this work we study the dependence $S_m = S_m(T)$.

Analogously to enthalpy, we are interested in branch GC. In Fig. 2a, the dependence $S_m = S_m(T)$ is monotonous on this branch, whereas in Fig. 2b, we observe the minimum E_1 and maximum E_2 . A qualitative difference exists between the behaviour depicted in Figs 2a and 2b. On isentropic cooling of a gas behaving according to Fig. 2a, we get into the two-phase region when crossing the line CG. The behaviour of gas in Fig. 2b is more complex: Let us have a gas whose entropy lies between the values given by the maximum and minimum. On isentropic cooling the gas, we get into the two-phase

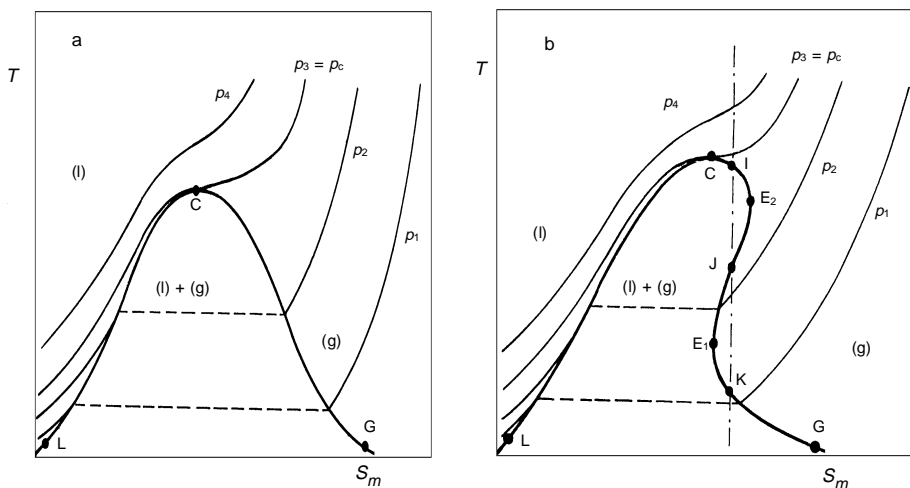


FIG. 2

Schematic sketch of $T = T(S)$ diagram. Symbol (g) denotes the gas region, symbol (l) the liquid region. Solid line without designation separates the region of homogeneous fluid from the two-phase region, (g) + (l). C is the critical point. Solid lines with designation p_i are isobars, the shape of isobars in the two-phase region is denoted by dash line. In a, entropy of saturated vapour as a function of temperature has no extreme. In b, E_1 is the minimum and E_2 the maximum of dependence of entropy of saturated vapour on temperature. The meaning of points G, I, J, K and L is explained in the main text. Dot-and-dash line designates isentropic cooling (see main text)

region at point I. On further cooling, we get again into the gas region at point J. If we cool the gas even more, we get again into the two-phase region at point K.

Let us investigate the dependence of entropy of saturated vapour on temperature corresponding to Fig. 2b. At extremes E_1 and E_2 we have

$$\left(\frac{dS_m}{dT}\right)_\sigma^{(g)} = 0 \quad (11)$$

This equation can be rewritten into the form (we proceed analogously to transforming Eq. (2) to Eq. (3))

$$0 = C_{pm}^{(g)} + T \left(\frac{\partial S_m}{\partial p}\right)_T^{(g)} \left(\frac{dp^\sigma}{dT}\right)_\sigma \quad (12)$$

If we write the heat capacity $C_{pm}^{(g)}$ in terms of Eq. (4) and denote by symbol ϕ_S the expression

$$\phi_S = -C_{pd}^{(g)} - T \left(\frac{\partial S_m}{\partial p}\right)_T^{(g)} \left(\frac{dp^\sigma}{dT}\right)_\sigma \quad (13)$$

we get the condition for extreme equivalent to Eq. (11)

$$C_{pm}^0(T) = \phi_S(T) \quad (14)$$

Let us discuss now the form of function ϕ_S in dependence on temperature. As has been said, the gas in the vicinity of the triple point behaves nearly as ideal gas. The values of $C_{pd}^{(g)}$ and $(dp^\sigma/dT)_\sigma$ are small here. However, for an ideal gas

$$\left(\frac{\partial S_m}{\partial p}\right)_T = -\frac{R}{p^\sigma}$$

is large and negative. Consequently, ϕ_S is here large and positive and

$$C_{pm}^0(T) < \phi_S(T) \quad (15)$$

applies.

At the critical point (points C in Fig. 2) we get

$$\lim_{T \rightarrow T_c} \left(\frac{dS_m}{dT}\right)_\sigma^{(g)} = -\infty \quad (16)$$

Therefore the function ϕ_S as well as ϕ_H has an infinitely high value at the critical point. In the vicinity of the critical point, the same inequality, relation (15), therefore holds as in the vicinity of the triple point.

Unlike with similar inequalities (7) and (10) for enthalpy, the existence of extreme does not follow from relation (15) for the temperature interval between the triple and critical points. The calculations (see next paragraph) of the dependence $\phi_S = \phi_S(T)$ in terms of the van der Waals and Redlich–Kwong equations of state, however, indicate that within the interval of temperatures investigated, $\phi_S = \phi_S(T)$ has a minimum. If relation (15) holds at all temperatures for the given substance, the entropy of saturated vapour as a function of temperature has not any extreme and behaves according to Fig. 2a. If in a certain temperature interval, ϕ_S is lower than the ideal-gas molar isobaric heat capacity, the entropy of saturated vapour has two extremes and behaves as it is outlined in Fig. 2b.

The described behaviour of ϕ_S is shown in Fig. 3 for propane and butane. It follows from the van der Waals equation that both the molar entropy of saturated vapour of propane and the molar entropy of saturated vapour of butane have a maximum and a minimum in dependence on temperature. On the other hand, the Redlich–Kwong equation of state predicts the existence of extremes only for butane and not for propane. It is possible to draw the following conclusions from the figure:

1. Function ϕ_S is sensitive to the equation of state chosen. Therefore, for its determination, it is necessary to employ an equation of state as accurate as possible.
2. The higher ideal-gas molar isobaric heat capacity has the substance, the more probable is the existence of the extremes. According to the principle of equipartition of energy, the ideal-gas molar isobaric capacity increases with the number of atoms in

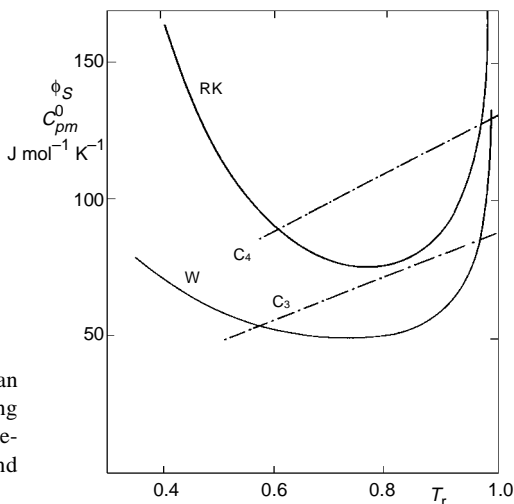


FIG. 3

Dependence $\phi_S = f(T_r)$ following from the van der Waals (W) and from the Redlich–Kwong (RK) equation of state (solid lines) and dependence $C_{pm}^0 = f(T_r)$ for propane (C₃) and butane (C₄) (dot-and-dash lines)

molecule. The existence of extremes is therefore to be expected rather with substances with polyatomic molecules.

3. If the ideal-gas molar isobaric heat capacity for the given substance is too high, one of points of intersection of functions $C_{pm}^0(T)$ and $\phi_S(T)$ may appear at a temperature lower than is the triple-point temperature and will be in this case non-physical. If this occurs, the dependence of entropy of saturated vapour on temperature will have only a maximum and no minimum.

Computation of ϕ_H and ϕ_S from Equations of State

Let us consider a general equation of state in the form

$$z = z(T, d) \quad , \quad (17)$$

where $z \equiv pV_m/RT$ is the compressibility factor and d the molar density. Let us introduce some auxiliary quantities which are related to the derivatives and integrals of the compressibility factor with respect to the state variables T and d (see refs^{5,6}):

$$Q_d = z + d \left(\frac{\partial z}{\partial d} \right)_T \quad (18)$$

$$Q_T = z + T \left(\frac{\partial z}{\partial T} \right)_d \quad (19)$$

$$Q_U = T \int_0^d \left(\frac{\partial z}{\partial T} \right)_d d \ln d \quad (20)$$

$$Q_C = T^2 \int_0^d \left(\frac{\partial^2 z}{\partial T^2} \right)_d d \ln d \quad . \quad (21)$$

For quantities ϕ_H and ϕ_S then holds (see ref.⁵)

$$\phi_H = -R \left[1 + 2Q_U + Q_C - \frac{Q_T^2}{Q_d} \right]^{(g)} + R z^{(g)} \left[\frac{Q_T}{Q_d} - 1 \right]^{(g)} \left[\frac{Q_U^{(l)} - Q_U^{(g)}}{z^{(g)} - z^{(l)}} + 1 \right] \quad (22)$$

$$\phi_S = -R \left[1 + 2Q_U + Q_C - \frac{Q_T^2}{Q_d} \right]^{(g)} + R \frac{z^{(g)} Q_T^{(g)}}{Q_d^{(g)}} \left[\frac{Q_U^{(l)} - Q_U^{(g)}}{z^{(g)} - z^{(l)}} + 1 \right] \quad . \quad (23)$$

All the quantities denoted by the superscript (g) are functions of temperature T and density of saturated vapour $d^{(g)} = d^{(g)}(T)$; the quantities denoted by the superscript (l) are functions of temperature and density of saturated liquid $d^{(l)} = d^{(l)}(T)$. The densities of saturated vapour and liquid for the given temperature can be calculated from an equation of state as well. The algorithm of their numerical computation for a general equation of state is given in Appendix.

RESULTS AND DISCUSSION

We derived the relation for maximum enthalpy of saturated vapour as a function of temperature, Eq. (6), and the relation for maximum and minimum of entropy of saturated vapour as a function of temperature, Eq. (14). From these equations, we can calculate the temperatures corresponding to the extremes providing we know the temperature dependence of heat capacity of a substance in the ideal-gas state and ϕ_H and ϕ_S as functions of temperature.

The dependences of heat capacities C_{pm}^0 on temperature are known for a great many substances, see ref.⁷. The functions ϕ_H and ϕ_S may, in principle, be determined from an arbitrary equation of state. The problem consists in the fact that these functions are considerably sensitive to the quality of equation of state as was demonstrated in Fig. 3. This is not surprising. From the equation of state, it is required here to express well the thermodynamic behaviour not only in the gas, but also in the liquid phase, see relations (22) and (23). Simple equations of state such as the van der Waals or Redlich–Kwong equations do not evidently meet this requirement. In current literature, the best equation of state is considered the Bender equation⁸ which describes the p – V – T behaviour in the gas and liquid phases with high accuracy. A disadvantage of this equation is the fact that the values of its constants are known only for about 30 substances (see refs^{8–16}). To be able to estimate the positions of extremes for a wide range of substances, we propose the procedure based on the theorem of corresponding states.

We shall assume that ϕ_H and ϕ_S are universal functions of reduced temperature, $T_r = T/T_c$ and acentric factor ω . Further we shall assume that their dependences on ω are linear

$$\phi_H(T_r, \omega) = \phi_H^{(0)}(T_r) + \omega \phi_H^{(1)}(T_r) \quad (24)$$

$$\phi_S(T_r, \omega) = \phi_S^{(0)}(T_r) + \omega \phi_S^{(1)}(T_r) . \quad (25)$$

To verify these assumptions, we computed ϕ_H and ϕ_S at three reduced temperatures and plotted them as functions of ω for the gases for which constants of the Bender equation

of state are known (argon, krypton, nitrogen, oxygen, carbon monoxide, carbon dioxide, water, sulfur hexafluoride, methane, ethane, ethene, propane, propene, propyne, cyclopropane, butane, 2-methylpropane, pentane, hexane, heptane, octane, benzene, toluene, methanol). The values of acentric factor were taken from the monograph by Reid *et al.*¹⁷. Figures 4 and 5 show that the relations (24) and (25) are satisfactorily precise.

We computed ϕ_H and ϕ_S for a number of reduced temperatures and determined $\phi_H^{(0)}(T_r)$, $\phi_H^{(1)}(T_r)$, $\phi_S^{(0)}(T_r)$, $\phi_S^{(1)}(T_r)$ by the least-square method. These quantities are given

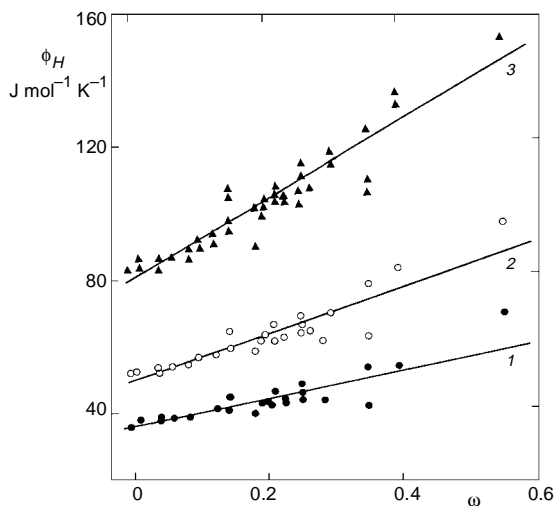


FIG. 4
Values of ϕ_H as functions of acentric factor ω computed in terms of the Bender equation of state for different substances at three reduced temperatures. 1 $T_r = 0.85$, 2 $T_r = 0.90$, 3 $T_r = 0.95$. Solid lines correspond to linear plot (24) with parameters from Table I

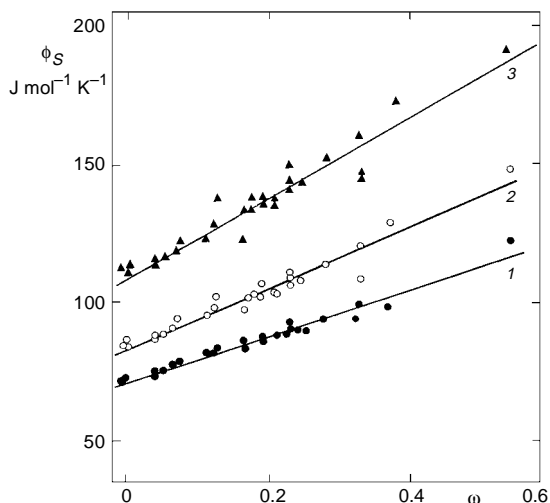


FIG. 5
Values of ϕ_S as functions of acentric factor ω computed in terms of the Bender equation of state for different substances at three reduced temperatures. 1 $T_r = 0.85$, 2 $T_r = 0.90$, 3 $T_r = 0.95$. Solid lines correspond to linear plot (25) with parameters from Table I

in Table I. Using the values in Table I and relations (24) and (25), it is possible to estimate ϕ_H and ϕ_S for every substance for which critical temperature and acentric factor are known.

From the literature dependences of ideal-gas heat capacity on temperature⁷ and using Eqs (6) and (14), we have computed the values of reduced temperatures corresponding to the extremes of enthalpy and entropy. The reduced temperatures corresponding to the maximum of molar enthalpy of saturated vapour calculated from relations (6) and (24) are compared in Table II with the values found in the literature. Deviations between the literature reduced temperatures and those estimated by us are typically about 0.01 and the maximum deviation is 0.03, which can be considered a good agreement. The differences among the results of different authors are approximately the same. We remark that the literature values are not the results of direct experiments but of calcula-

TABLE I
Parameters of linear regression relations $\phi_H^{(0)}$, $\phi_H^{(1)}$, $\phi_S^{(0)}$, $\phi_S^{(1)}$ ($\text{J mol}^{-1} \text{K}^{-1}$) in dependence on reduced temperature $T_r = T/T_c$ determined for the estimation of ϕ_H and ϕ_S according to relations (24) and (25). Values of $\phi_H^{(0)}(T_r)$ and $\phi_H^{(1)}(T_r)$ for $T_r \leq 0.65$ are not given in this table for at these temperatures $C_{pm}^{(0)}$ is always larger than ϕ_H

T_r	$\phi_H^{(0)}$	$\phi_H^{(1)}$	$\phi_S^{(0)}$	$\phi_S^{(1)}$
0.40			147.3	137.7
0.45			122.5	100.5
0.50			97.2	118.2
0.55			86.4	105.8
0.60			79.2	93.2
0.65			74.2	84.3
0.70	15.2	2.7	70.9	78.3
0.75	20.8	6.9	69.8	76.7
0.80	27.3	19.4	70.5	79.6
0.85	35.9	38.2	73.8	88.5
0.90	49.7	66.3	82.3	106.9
0.925	61.3	88.4	91.3	118.6
0.95	80.4	116.1	108.0	141.1
0.975	126.4	173.4	150.2	192.7
0.98	144.8	196.8	168.0	214.3
0.99	214.7	293.4	235.5	308.4

TABLE II

Literature values of reduced temperature T_r^{\max} corresponding to the maximum of enthalpy of saturated vapour and its estimates $T_{r,\text{est}}^{\max}$ according to Eqs (6) and (24)

Substance	T_r^{\max}	Ref.	$T_{r,\text{est}}^{\max}$
Neon	0.743	18	0.750
Argon	0.759	18	0.750
	0.743	19	
Nitrogen	0.804	18	0.804
	0.808	20	
	0.800	19	
Oxygen	0.804	18	0.810
Fluorine	0.771	18	0.805
Chlorine	0.846	18	0.826
Carbon monoxide	0.836	18	0.806
	0.784	21	
Water	0.777	18	0.808
	0.784	22	
Carbon dioxide	0.788	18	0.813
	0.826	19	
Ammonia	0.801	18, 19	0.824
Methane	0.840	18	0.840
	0.837	23	
	0.795	19	
	0.829	20, 24	
Chlorodifluoromethane	0.913	18	0.888
Dichlorodifluoromethane	0.922	18	0.926
Chlorotrifluoromethane	0.910	18	0.904
Ethane	0.867	18, 19	0.880
	0.874	24	
	0.881	25	
Ethyne	0.839	19	0.842
1,1-Difluoroethane	0.914	26	0.913
1,1,2,2-Tetrafluoroethane	0.933	27	0.930
2,2-Dichloro-1,1,1-trifluoroethane	0.959	28	0.960
Propane	0.940	18, 19	0.936
	0.934	24	
	0.920	29	

TABLE II
(Continued)

Substance	T_r^{\max}	Ref.	$T_{r,\text{est}}^{\max}$
Propene	0.916	29	0.920
Butane	0.962	24	0.968
	0.950	29	
2-Methylpropane	0.959	24	0.965
	0.963	29	
2-Methylprop-2-ene	0.960	29	0.957
Octafluorocyclobutane	0.977	18	0.973
Benzene	0.982	18	0.978
Methanol	0.829	18	0.842
	0.832	30	

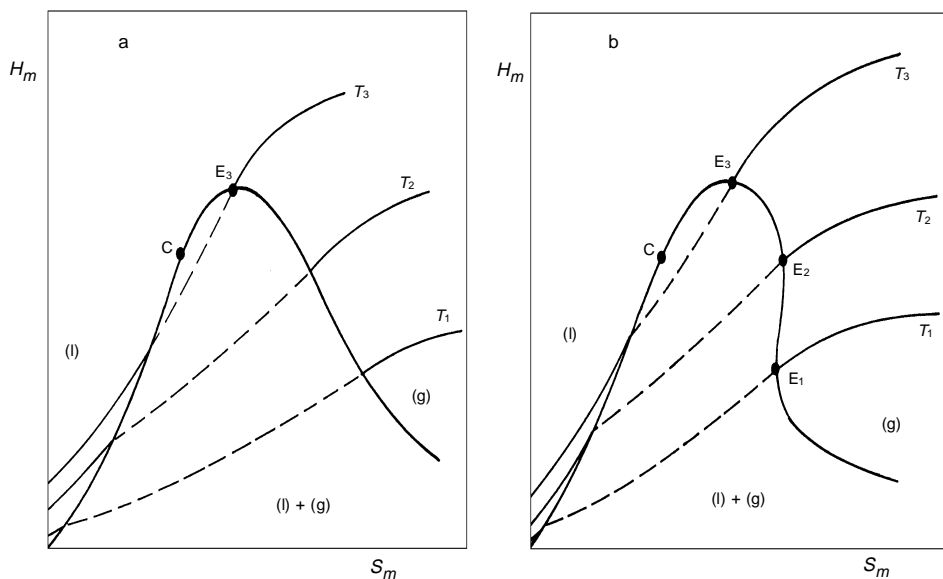


FIG. 6

Schematical sketch of $H_m = H_m(S_m)$ diagram. Symbol (g) denotes the gas region, symbol (l) the liquid region. Solid line without designation separates the region of homogeneous fluid from the two-phase region, (g) + (l). C is the critical point. Solid lines with designation T_i are isotherms, the shape of isotherms in the two-phase region is denoted by dash line. In a, the entropy of saturated vapour as a function of enthalpy of saturated vapour has no extreme. In b, E_1 is the minimum and E_2 the maximum of dependence of entropy of saturated vapour on its enthalpy

tions from the p - V - T behaviour. Therefore, it is not possible to say whether they are more accurate than our estimates.

The reduced temperatures corresponding to the minimum and maximum of entropy of saturated vapour calculated from relations (14) and (25) with the values found in literature are compared in Table III. The same conclusions are valid here as with values in Table II even if the number of substances, for which extremes were found, is much smaller. It is interesting that in the Hanson tables²⁹, one does not find any minimum for butane, 2-methylpropane and butene, and that the temperatures of maximum rather differ both from recent results¹⁰ and from our estimates. The estimation method proposed by us seems to be capable of serving as a test of accuracy of the published tables and diagrams.

In addition to the H - p and T - S diagrams, one often meets in applied thermodynamics with the H - S diagram, too. The results of this work can be applied even to this diagram which is schematically illustrated in Fig. 6. In this figure, three subcritical isotherms and the curve separating the homogeneous and heterogeneous regions are plotted. Analogously to the T - S diagram, see Fig. 2, this curve may look such as it is outlined in Fig. 6a or such as it is indicated in Fig. 6b. It is possible to show that for the temperature at which $H_m = H_m(S_m)$ has a maximum, *i.e.*, at point E_3 , the condition (6) is valid. This maximum occurs with all substances. For the temperatures when $S_m = S_m(H_m)$ has two extremes, *i.e.*, the points E_1 and E_2 , condition (14) holds, the extremes occurring only with some substances. With the substances for which relation (15) holds at all temperatures between the triple and critical points, the dependence of entropy of saturated vapour on its enthalpy is monotonous.

TABLE III

Literature values of reduced temperatures corresponding to the minimum T_r^{\min} and maximum T_r^{\max} of entropy of saturated vapour and their estimates $T_{r,\text{est}}^{\min}$, $T_{r,\text{est}}^{\max}$ in terms of relations (14) and (25)

Substance	T_r^{\min}	T_r^{\max}	Ref.	$T_{r,\text{est}}^{\min}$	$T_{r,\text{est}}^{\max}$
2,2-Dichloro-1,1,1-trifluoroethane	0.631	0.926	28	0.635	0.922
Butane	0.641	0.941	24	0.638	0.938
	–	0.908	29		
2-Methylpropane	0.662	0.932	24	0.653	0.934
	–	0.898	29		
2-Methylprop-2-ene	–	0.870	29	0.686	0.912
	0.613	0.972	18	0.616	0.954

APPENDIX

Computation of Density of Saturated Vapour $d^{(g)}$ and Density of Saturated Liquid $d^{(l)}$ from Equations of State

For the chosen temperature T , the first step of calculation consists in solving the conditions of phase equilibrium which require the equality of pressures and fugacities in both the phases, *i.e.*,

$$p^{(g)}(T, d^{(g)}) = z(T, d^{(g)}) RTd^{(g)} = z(T, d^{(l)}) RTd^{(l)} = p^{(l)}(T, d^{(l)}) \quad (A1)$$

$$f^{(g)}(T, d^{(g)}) = f^{(l)}(T, d^{(l)}) , \quad (A2)$$

where $d^{(g)} = 1/V_m^{(g)}$ and $d^{(l)} = 1/V_m^{(l)}$ are the molar densities in the vapour and liquid phase, respectively. This system of equations was solved by the Newton–Raphson method

$$\left(\frac{\partial p}{\partial d} \right)_T^{(g)} \Delta d^{(g)} - \left(\frac{\partial p}{\partial d} \right)_T^{(l)} \Delta d^{(l)} = p_I^{(l)} - p_I^{(g)} \quad (A3)$$

$$\left(\frac{\partial f}{\partial d} \right)_T^{(g)} \Delta d^{(g)} - \left(\frac{\partial f}{\partial d} \right)_T^{(l)} \Delta d^{(l)} = f_I^{(l)} - f_I^{(g)} , \quad (A4)$$

where p_I and f_I are the approximations of pressures and fugacities, respectively, obtained with the I -th approximation of densities in the liquid or gas phase. After corresponding rearrangements and on using the dimensionless Q -quantities⁵, this system of equations can be rearranged into the form⁶

$$Q_d^{(g)} \Delta d^{(g)} - Q_d^{(l)} \Delta d^{(l)} = z^{(l)} d^{(l)} - z^{(g)} d^{(g)} \quad (A5)$$

$$\begin{aligned} [Q_d \exp(Q_F + z - 1)]^{(g)} \Delta d^{(g)} - [Q_d \exp(Q_F + z - 1)]^{(l)} \Delta d^{(l)} = \\ = [d \exp(Q_F + z - 1)]^{(l)} - [d \exp(Q_F + z - 1)]^{(g)} , \end{aligned} \quad (A6)$$

where Q_d is defined by relation (18) and for Q_F we have

$$Q_F = \int_0^d (z - 1) d \ln d . \quad (A7)$$

The first approximation of density of the liquid phase (at $T_r = 0.8$) was determined according to the Rackett equation¹⁷. The density in the vapour phase (at $T_r = 0.8$ as well) was estimated in terms of the ideal-gas equation of state with the saturated vapour pressure estimated from the relation $\ln(p^0/p_c) = 7(1 - 1/T_r)$. At the other temperatures, the results were used obtained in preceding iteration step. Further details can be found in ref.⁶.

As soon as the increments in densities of single phases were sufficiently low, the iteration process was finished, and ϕ_H and ϕ_S were calculated from relations (22) and (23). Usually about 5 to 8 iterations were necessary (on changing reduced temperature by 0.05).

SYMBOLS

C_{pm}	molar isobaric heat capacity
C_{pm}^0	molar isobaric heat capacity of ideal gas
C_{pd}	molar departure isobaric heat capacity, Eq. (4)
d	molar density
f	fugacity
H_m	molar enthalpy
p	pressure
p_c	critical pressure
p^0	saturated vapour pressure
Q_b, Q_T, Q_U, Q_C	see Eqs (18)–(21)
Q_F	see Appendix
R	molar gas constant
S_m	molar entropy
T	temperature
T_c	critical temperature
T_r	reduced temperature
V_m	molar volume
z	$\equiv pV_m/RT$, compressibility factor
ϕ_H	see Eq. (5)
$\phi_H^{(0)}, \phi_H^{(1)}$	see Eq. (24)
ϕ_S	see Eq. (13)
$\phi_S^{(0)}, \phi_S^{(1)}$	see Eq. (25)
ω	acentric factor

Superscripts

(g)	gas phase
(l)	liquid phase
min	minimum
max	maximum

Subscripts

σ	saturated vapour
est	estimated

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