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BRIEF COMMUNICATIONS

New Equation of Boiling Curve

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Abstract—A dependence of a saturated vapor pressure of individual substances on a temperature describing this whole curve was obtained by coordinates of two points on the boiling curve thereby one of these points was critical.

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The boiling curve represents the dependences of the saturated vapor pressure P_{sv} (Pa) of the individual substances on the temperature T (K) or the dependence of the boiling temperature T_b (K) on the pressure P (Pa). In coordinates T–P the boiling curve limited by the critical point coordinates (T_{cr} and P_{cr}) where a boundary between gas and liquid phases disappears, on the one side and by coordinates of a triple point where a curves of boiling (condensation), sublimation, and melting (solidification) come together, on the other side.

Operating with chemicals a relation of the saturated vapor pressure and temperature is used for governing partial pressure of appropriate substances in obtained gas mixtures, and also for providing flame safety and maximum permissible concentrations in a room. For noted targets a reliable and accessible information is required not as discrete experimental points on the boiling curve but as generalized equation involving a total range of conditions when gas–liquid transfer occurs.

All attempts to apply the Clausius–Clapeyron relation for description of the boiling curve resulted by obtaining semi-empirical equations for the independent curve sections [1]. A set of the standard conditions in the equation (2) results in an inevitable exclusions and large errors for some substances.

A development of a way for description of the whole boiling curve that requires minimum initial experimental data is the purpose of our report.

We found that in $\ln(P_{sv}\ T_b\ )$–$1/\ T_b$ coordinates the boiling curves of all substances became straight and can be simulated by equitype equation looking as

$$P_{sv}T_b = P_{cr}T_{cr} \exp\,[-(\Delta H/R)(1/T_b - 1/T_{cr})], \qquad (1)$$

where $R = 8.314$ J mol^{-1} K^{-1}, ΔH was enthalpy of evaporation (J mol^{-1}), constant value in a range of the parameters P_{sv} and T_b from the critical point to triple one.

At solution of equation (1) with respect to ΔH its value can be computed by coordinates of two points, one of which is critical:

$$\Delta H = R\,(1/T_b - 1/T_{cr})^{-1} \ln\,[P_{cr}T_{cr}/(P_{sv}\ T_b)]. \qquad (2)$$

The computed enthalpy of evaporation of the some substances with use in equation (2) in addition to the values of T_{cr}, and P_{cr}, normal values of the boiling temperature (T_{nb} at 101.325 kPa) or parameters of the triple point, i.e. for a temperature range from T_{cr} to T_{nb} or for the whole boiling curve are preseted in the table. The used values of P_{cr}, T_{cr}, and T_{nb} are from [1], the parameters of the triple point from [3]. Inorganic and organic substances, monoatomic and polyatomic ones, and also non-polar and polar substances including those that do not possess T_b (CO_2, C_2H_2, $AlCl_3$) are listed in the table.

An average deviation Δ (%) of two computed values of ΔH from each other (for 18 substances) is less than 0.7 rel % and that does not exceed an error of parameters used for the calculation **(**according to data of [1], deviation for T_{cr} equals ±(0.5–1.5)%, for P_{cr} ±(1–3)%**)**. That evidences a constancy of ΔH value in the total range of conditions for the gas–liquid transfer.

The characteristics of the boiling curve

Substance	Point on curve	Parameters of the point		ΔH, kJ mol^{-1}, equation (2)	Δ, %
		P_{sv}, Pa	T_b, K		
Ne	Critical	2653000	44.40		
	Normal	101325	27.09	2.17	0.9
	Triple	43260	24.54	2.15	
Ar	Critical	4866000	150.65		
	Normal	101325	87.3	7.62	0.1
	Triple	68900	83.81	7.61	
N_2	Critical	3398000	126.19		
	Normal	101325	77.35	6.65	0.5
	Triple	12520	63.14	6.62	
O_2	Critical	5046000	154.58		
	Normal	101325	90.19	8.00	0.4
	Triple	156	54.36	7.97	
Cl_2	Critical	7977000	416.9		
	Normal	101325	239.2	22.96	–1.5
	Triple	1354	172.1	23.31	
Br_2	Critical	10330000	584.0		
	Normal	101325	331.9	33.17	–3.7
	Triple	4655	265.9	34.46	
CO	Critical	3500000	132.85		
	Normal	101325	81.64	7.09	0.0
	Triple	15370	68.13	7.09	
HCl	Critical	8260000	324.7		
	Normal	101325	188.1	18.39	–0.2
	Triple	13700	159.0	18.43	
H_2O	Critical	22060000	647.20		
	Normal	101325	373.15	43.48	–2.5
	Triple	609	273.16	44.64	
H_2S	Critical	8970000	373.3		
	Normal	101325	212.9	20.78	–0.3
	Triple	23200	187.61	20.84	
H_2Se	Critical	8850000	410.6		
	Normal	101325	231.8	22.31	1.1
	Triple	27300	207.43	22.07	

Table (Contd.)

Substance	Point on curve	Parameters of the point		ΔH, kJ mol^{-1}, equation (2)	Δ, %
		P_{sv}, Pa	T_b, K		
NH_3	Critical	11350000	405.46		
	Normal	101325	239.82	25.59	–1.2
	Triple	6080	195.43	25.91	
PH_3	Critical	6530000	325.0		
	Normal	101325	185.7	17.02	0.6
	Triple	3640	139.4	16.92	
AsH_3	Critical	6790000	375.0		
	Normal	101325	210.7	19.12	–0.2
	Triple	2978	156.23	19.16	
SiH_4	Critical	4840000	269.5		
	Normal	101325	161.2	14.61	1.2
	Triple	28	88.48	14.43	
CH_4	Critical	4600000	190.6		
	Normal	101325	111.66	9.75	0.7
	Triple	11540	90.67	9.68	
C_2H_2	Critical [4]	6400000	308.35		
	Triple	128200	192.6	18.69	–
C_2H_4	Critical [3]	5042000	282.35		
	Normal [3]	101325	169.43	15.56	–2.3
	Triple	120	103.94	15.93	
$AlCl_3$	Critical	5480000	628.3		
	Triple [3]	231000	465.6	51.8	–
	Triple [4]	228000	465.6	52.0	(0.4)
CO_2	Critical	7377000	304.14		
	Triple	516000	216.6	18.77	–
Re_2O_7	Critical	6890000	942		
	Normal	101325	631.7	73.65	–2.0
	Triple	24500[a]	574.6	75.13	

[a] Erratum in [3].

Enthalpy of evaporation of appropriate substance should be computed by equation (2) for obtaining all necessary constants in order to use equation (1) as the dependence of the saturated vapor pressure on the temperature, that is:

$$P_{sv} = (P_{cr}T_{cr}/T) \exp [-(\Delta H/R)(1/T - 1/T_{cr})],$$

where the pre-exponential factor is inversely proportional to the temperature.

It should be noted that the value of enthalpy of evaporation ΔH from equation (1) is larger than the heat of boiling for the appropriate substance measured at the temperature T_{nb} approximately by value of RT_{nb}.

CONCLUSIONS

(1) It was demonstrated that only the coordinates for two points of the curve thereby one of these points is critical, are required for description of the whole boiling curve of various substances.

(2) The dependences of the saturated vapor pressure on the temperature when heat of evaporation was constant in the total range of conditions of the liquid phase existence and the pre-exponential factor was inversely proportional to the temperature were obtained.

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