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18 October 1960

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PROPERTIES OF PROPYLENE

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- USSR -

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/Following is the translation of an article by Ya. Z. Kazavchinskiy and V. A. Zagoruchenko entitled "Uravneniye Sostoyaniya i Termodinamicheskiye Svoystva Propilena" (English version above) in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol. XXXIII, No. 3, 1959, pages 662-664./

THE EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF PROPYLENE

Ya. Z. Kazavchinskiy and V. A. Zagoruchenko (Odessa)

S u m m a r y

In the present report an equation of state for propylene is proposed, based on the most recent p, v, t data. The equation holds for all temperatures of practical importance within the limits of reduced density $\omega=0-3.13$, the saturation curve up to $\omega=2.6$ also being satisfied. Thus for the first time an equation of state has been obtained which is valid both for the liquid and gaseous regions, realizing not only qualitatively, but also quantitatively the idea of the continuity in the transition from the liquid to the gaseous phase.

The equation depicts the thermal and caloric properties of propylene with a high degree of accuracy and is in agreement with the critical point, the critical conditions and also all other basic conditions that should be satisfied by a rational equation of state for a real gas. The equation may be used for tabulating in detail the thermodynamic properties of propylene.

The equation of state for propylene was set up according to an earlier-described method [1], and has the following form in dimensionless coordinates:

$$\sigma = \alpha_0 + \alpha_1 \tau + \beta \phi, \quad (1)$$

where σ is a dimensionless complex equal to $p v / R T_k$; α_0 , α_1 , β are elementary functions of the equation depending on the normalized density $\omega = v_k / v$; and ϕ is an elementary function depending only on the normalized temperature $\tau = T / T_k$.

From the analysis of the experimental p , v , T data of Michels and Wassenaar [2], Vaughan and Graves [3], and Marchman with coauthors [4,5], it was established by us that the temperature function for propylene can be represented with a sufficient degree of precision in the form:

$$\phi = \frac{1}{\tau^3}.$$

Further on, knowing in the coordinates σ , ω the equations of three isotherms (according to the number of the volumetric elementary functions α_0 , α_1 , β) and having an analytical expression for ϕ , it is possible to obtain very simply in an analytical way the expression for α_0 , α_1 and β .

In setting up the equation of state for propylene, the equations of isotherms found by Michels [2] for 100, 125 and 150°C were used, which were converted by us into dimensionless units. With this, the value of the critical temperature, viz.: $t_k = 91.9^\circ\text{C}$, was taken by us according to Rossini's [6] data; the critical density and critical pressure were found by studying isochoric cross-sections of the experimental p, v, T data of Michels [2], whose investigations, as is known, show a high accuracy. A rectilinear isochor at a density of $d_A = 108.84$ Amaga units (which corresponds to 0.2081 g/cm^3) was discovered. Since in the overwhelming number of real gases, including ethane, propane, isobutane and neopentane, a critical isochor is formed by a straight line, then also in propylene the value of density corresponding to a rectilinear isochor is taken as the critical one. This was used for calculating p_k , which was found to be equal to 45.60 atm, actually coinciding with the value of 45.61 atm found by Marchman [5].

With accepted values of critical parameters, the critical number is

$$k = \frac{p_k v_k}{RT_k} = 0.30829.$$

Using the isothermic equations and performing the necessary operations, in conformity with the methods exposed in the above-mentioned work [1], we have found the following expressions for the elementary functions of equation (1):

$$\begin{aligned} \alpha_0 &= -1,606073 \omega - 1,117667 \omega^2 + 9,700514 \omega^3 + 19,823288 \omega^4 + \\ &\quad + 17,507010 \omega^5 - 7,756692 \omega^6 + 1,700014 \omega^7 - 0,146421 \omega^8; \\ \alpha_1 &= 1 + 0,693540 \omega + 1,062298 \omega^2 - 6,796533 \omega^3 + 13,561286 \omega^4 - \\ &\quad - 11,870716 \omega^5 + 5,252110 \omega^6 - 1,450251 \omega^7 + 0,099073 \omega^8; \\ \beta &= -0,203874 \omega + 0,511331 \omega^2 - 3,128434 \omega^3 + 6,871266 \omega^4 - \\ &\quad - 6,322385 \omega^5 + 2,841779 \omega^6 - 0,623130 \omega^7 + 0,053447 \omega^8. \end{aligned}$$

The proposed equation of state for propylene with the expressions found for α_0 , α_1 and β transmits with high accuracy the thermal properties not only at 100, 125 and 150°C, which data were taken as a basis for the setup of the equation, but also admits a wide extrapolation into the region of high and low temperatures. Thus, for example, the comparison of the experimental and calculated ϵ which was effected, showed a good coincidence both on the side of the gas ($\omega < 1$) and on the side of the liquid ($\omega > 1$). At 25, 50 and 75°C, the average deviations between experimental and calculated values constitute 0.080, 0.073 and 0.055%, respectively; maximal deviations in this case do not exceed 0.18%. It is interesting to note that in a number of cases, at subcri-

tical temperatures, on the side of a liquid ($\tau < 1, \omega > 1$) the equation of state better satisfies the experimental data of Michels than the equations of isotherms specially set up by him for these temperatures. For example, at 88.2°C the average deviation between the experimental values of σ and calculated ones in relation to the equation of state constitutes 0.32%, and that between experimental and calculated values in regard to the equation set up by Michels only for this temperature, in the interval $\omega = 1.5 \div 3.1$, constitutes 0.41%.

The equation of state fully satisfies the critical point (at $\tau = 1$ and $\omega = 1$, $\sigma_k = 0.30829$) and the derivative at a critical point with an accuracy of 1.25% ($\sigma_k' = -0.3121 = -1.0125 k$), and also satisfies the saturation curve. The comparison of thermal values on the saturation curve according to data [4] with calculated values according to the equation of state, effected in the table, showed that in the whole range of variations of densities of $\omega = 0-2.5$, the error δ between tabular and calculated values of specific volumes v on the boundary curves does not exceed 1%; with a density of $\omega = 2.6$, the divergence reaches 4%. For this reason, the equation of state for propylene may be used on the saturation curve only up to $\omega = 2.5$.

Comparison of values of specific volumes on the saturation curve found according to the equation of state (1) with the tabular data of Marchman [4]

t, °C	p, atm	v', l/kg		δ , %	v'', l/kg		δ , %
		[4]	(1)		[4]	(1)	
-47,70	1,000				6,774	6,768	-0,089
-40,00	1,401				4,959	4,955	-0,081
-28,89	2,187				3,284	3,274	-0,396
-12,22	3,932				1,885	1,881	-0,212
-1,41	5,575	1,820	1,788	1,76	1,343	1,345	-0,149
10,00	7,685	1,880	1,859	1,13	0,976	0,981	-0,512
28,67	11,888	1,980	1,973	0,379	0,624	0,629	-0,801
37,78	15,486	2,062	2,060	0,097	0,472	0,475	-0,636
48,89	19,814	2,165	2,163	0,092	0,360	0,360	0
60,00	24,978	2,310	2,296	0,606	0,274	0,274	0
76,67	34,547	2,620	2,615	0,191	0,170	0,169	-0,588
87,78	42,385	3,110	3,110	0	0,106	0,105	-0,943

A comparison was also made between the values of σ calculated according to the equation of state and the experimental values of Vaughan and Graves [3] at 250°C; the average deviation is 0.161%, and maximal deviation reaches 0.48% (at the last experimental point). This confirms the validity of the proposed equation in the region of high temperatures as well.

In order to verify the equation of state according to the caloric data, the values $U - U_0$ and $C_v - C_{v\infty}$ were calculated and compared with the values found [2]. The calculations showed that the average divergence according to $U - U_0$ within the interval of 100-150°C is

0.05-0.42%, while according to $C_V - C_{V\infty}$ it reaches 25%. The observed divergences according to $C_V - C_{V\infty}$ are apparently explained by the inaccuracy of the data arrived at by Michels, because for finding the caloric values he used a graphic method for obtaining the first and second derivative with respect to the temperature, $(\partial p / \partial T)_V$ and $(\partial^2 p / \partial T^2)_V$, which does not ensure the necessary accuracy. Also, by the inaccuracy of the method adopted by Michels, the fact is explained that the divergence with respect to the intrinsic energy, in the determination of which only the first derivative, $(\partial p / \partial T)_V$, is used, proves to be smaller than with respect to the thermal capacity of $C_V - C_{V\infty}$, where the second derivative, $(\partial^2 p / \partial T^2)_V$, is used. It is interesting to note that the smallest divergences occur in the middle of the temperature range, while the greatest divergences take place at the ends of the temperature range which, naturally, is also caused by graphic differentiation.

Conclusions

1. The obtained equation of state for propylene is valid at all temperatures of practical importance in the region of a change of the indicated density of $\omega =$

= 0-3.13 and describes with high accuracy the thermal, as well as caloric, properties of the given substance.

2. The equation may be used for compiling detailed tables of thermodynamic properties of propylene necessary for engineering calculations.

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