Experimental determination of destruction of thermally unstable substances

T A-G Dzhapparov, A R Bazaev

Institute for Geothermal Research of the Daghestan Scientific Center of the Russian Academy of Sciences, Shamil 39A, Makhachkala, Daghestan Republic, 367030, Russia
E-mail: timur507@mail.ru

Abstract. Different methods of thermal stability determinations are reviewed. The process of thermal decomposition of aliphatic alcohols and their aqueous mixtures in the range of temperatures 583.15–663.15 K was studied using the method of isothermal pressure increasing in a closed system. The decomposition points (Td) alcohols dissolved in water are obtained depending on their concentration. The changes of thermal coefficients (isothermal coefficient of compressibility kT, coefficient of cubical expansion α and thermal coefficient of pressure β) and main thermodynamic properties (Cv, Cp, H, S, U, F, G) of studied mixtures depending on isothermal pressure increasing during the thermal decomposition of alcohols were calculated.

There is no definite opinion in the question of criteria of thermal stability of substances, as well as no definite technique of its estimation. Measure of the thermal stability of any substance is the temperature at which thermal decomposition starts and change of the chemical and physical properties begins. And determination of that temperature (decomposition point) is difficult because of some circumstances caused by the lack of definite factors of pyrolytic decomposition degree [1–3].

Some authors of the experimental works given in the internet use the methods of change of color and viscosity to determine thermal stability of substances, some authors also use pressure of gas products during decomposition of main substance [1–17]. Some authors believe [5–16] that method of isothermal pressure increase in the closed system is the most reliable for thermal stability determination. Particularly this method was used to estimate the decomposition points of liquid working agents. Authors of work [14] wrote that the temperature at which the rate of the thermal decomposition has the value 1.87 Pa/s is the decomposition point of the substance. In work [17] theoretical research of thermal stability and also theoretical determination of decomposition temperature are given. Author wrote that a decomposition temperature is defined as that temperature where 1 mole %, of the material decomposes per hour. In work [18] thermal stability of naphtene hydrocarbons by using method of pressure increasing at constant pressure in isoteniscope of high pressure. Authors made a conclusion that the value of decomposition temperature of cyclic hydrocarbons decreases with increasing number of cycles and for linear hydrocarbons the value of decomposition temperature decreases with increasing number of carbon atoms of hydrocarbon. The same technique was used in the work [19,20], at which thermal stability of n-pentane, cyclopentane, and toluene was investigated.

The measurements were performed in the next way. Nearcritical amount of sample was inserted into vacuumed constant volume piezometer and after that series of temperature were
Figure 1. Nearcritical isochore of pressure dependence of ethanol from temperature: 1 – pressure measured during 30 minutes after reaching thermodynamic equilibrium; 2 – pressure measured after 48 hours.

Figure 2. Nearcritical isochore of pressure dependence of ethanol from temperature: 1 – pressure measured during minutes after reaching thermodynamic equilibrium; 2 – pressure measured 5 hours.

In order to eliminate the isothermal rise of pressure, related with phase transition (liquid–gas–liquid and liquid–gas–gas) measurements were made along nearcritical isochores. The temperature of the experiment was measured by resistance thermometer of first class (PTS-10M) and controlled by high-precision temperature regulator (OWEN – TRM500, accuracy class 0.25). The pressure of the system was measured by pressure strain gauge (D-100). After reaching thermodynamic equilibrium the pressure of the system was measured every 1 hour during a long period of time (24–48 h). If there was no pressure increasing temperature would had been raised for 5 degrees and experiment was repeated. The procedure of determination of decomposition temperature was repeated 3 times. The standard uncertainties on the temperature of ±0.002%, pressure ±0.05%, and density ±0.15%. More detailed information about the technique of experiment is given in our earlier work [21,22]. Figures 1 shows nearcritical isochore of pressure – temperature dependence of ethanol for different period of time.

When there is no thermal decomposition of alcohol molecules the dependence of saturated pressure from temperature presents a smooth curve in every point. The rate of thermal decomposition of alcohols can be defined as change of pressure in a unit of time. Degree of the thermal decomposition of alcohols depends on time of temperature affect (figure 2). The data about thermal stability of pure and dissolved in water alcohols is contradictory so it must be specified [23–26]. It is found out that thermal decomposition temperature of alcohol molecules depends on structure, concentration and temperature impact duration. Values of the decomposition points (Td) were found by determining the kink on p-T curve during a long time period of temperature impact (48 hours). First three alcohols (methanol, ethanol and 1-propanol) are stable at temperatures higher than those of critical ones and 1-butanol starts to decompose at temperature lower than those of critical one (table 1 figure 3). Critical temperatures of pure alcohols, given on table 1 are taken from works [27,28].

At $T > T_d$ the rate of the thermal decomposition of alcohols as change of pressure $\Delta p$ in a unit of time $\Delta \tau$, i.e. $(\Delta p/\Delta \tau)H$ is estimated. It is shown that the value of $(\Delta p/\Delta \tau)H$ increases
Table 1. Decomposition temperatures of alcohol molecules in their water mixtures.

| x, mole frac. | Water-methanol | Water-ethanol | Water-1-propanol | Water-1-butanol |
|---------------|----------------|---------------|------------------|----------------|
| 1             | T_{cr} = 512.6 ± 0.3 | T_{cr} = 513.9 ± 0.3 | T_{cr} = 536.8 ± 0.3 | T_{cr} = 563.1 ± 0.3 |
| 0.8           | 523.15 ± 0.5     | 533.15 ± 0.5   | 548.15 ± 0.5     | 563.15 ± 0.5   |
| 0.5           | 533.15 ± 0.5     | 543.15 ± 0.5   | 558.15 ± 0.5     | 573.15 ± 0.5   |
| 0.2           | 548.15 ± 0.5     | 558.15 ± 0.5   | 573.15 ± 0.5     | 588.15 ± 0.5   |

with temperature and concentration of alcohol and decreases with number of carbon atom of alcohols (figure 4).

Isothermal rise of pressure effects the character of thermal coefficients change (isothermal compression coefficient \(k_T\), coefficient of volumetric expansion \(\alpha\), thermal coefficient of pressure \(\beta\)), and thermodynamic properties \((C_v, C_p, H, S, U, F, G)\). For the estimation of influence of thermal decomposition of alcohols on the thermodynamic properties of their water mixtures in the temperature range 583.15–663.15 K, the Redlich–Kwong equation of state was used [29]:

\[
P = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V + b)},
\]

\(V\) – molar volume of constant composition mixture that is equal to \((1 - x)V_1 + xV_2\), \(n_3/\text{mol}\), \(V_1, V_2\) – molar volumes of water and alcohol at temperature \(T\) and pressure \(p\), \(R = 8.314\ \text{J/(mol·K)}\) – is the gas constant, \(a\) is a constant that corrects for attractive potential of molecules, and \(b\) is a constant that corrects for volume. Average relative deviation between the measured and calculated values of pressure is less than 2.3%.

For calculation the values of thermal coefficients \((k_T, \alpha, \beta)\) and isothermal changes of the thermodynamic functions of water – aliphatic alcohol binary mixtures (isochoric and isobaric heat capacities \(C_v\) and \(C_p\), enthalpy \(S\), entropy \(H\), internal energy \(U\), free energy \(F\), Gibbs
Figure 5. Dependence of $\alpha$ from $T$ of water-1-propanol mixture ($x = 0.5$ mol. fraction) for different periods of time: 1 – in the beginning; 2–6 – after 1, 2, 3, 4, 5 hours respectively.

Figure 6. Dependence of $\beta$ from $T$ of water-1-propanol mixture ($x = 0.5$ mol. fraction) for different periods of time $\tau$: 1 – in the beginning; 2–6 – after 1, 2, 3, 4, 5 hours respectively.

energy $G$ relative to standard state ($p = 0.1$ MPa and $T = 583.15–663.15$ K) of expressions [30] were used.

The values of coefficients of equation 1, calculated by less square method are given on table 2 and the values of pressure change during 5 hours are shown on table 3.

Table 2. The values of coefficients of equation (1) for water–1-propanol mixture ($x = 0.5$) change during 5 hours.

| Time, min | $a$, $10^{-6}$Hm$^2$K$^{0.5}$/mol$^2$ | $b$, cm$^3$/mol |
|-----------|--------------------------------------|----------------|
| 0         | 29623139.10                          | 55.70          |
| 60        | 32041437.10                          | 59.42          |
| 120       | 34475206.86                          | 62.82          |
| 180       | 36922556.66                          | 65.95          |
| 240       | 39381891.08                          | 68.83          |
| 300       | 41851855.21                          | 71.49          |

As one can see values of thermal coefficients $\alpha$ and $\beta$ of water–1-propanol mixture ($x = 0.5$ mole fraction) have the same pattern according to temperature and differs according to curing time $\tau$: $\alpha$ and $\beta$ decreases by temperature and $\alpha$ decreases during time, but $\beta$ increases.

Figures 7 and 8 show the dependences of the values $H$ and $F$ for water–1–propanol mixture ($x = 0.5$ mole frac.). As one can see the pattern of isothermal changes of $F$ and $H$ for is the same: the values of $F$ and $H$ increases with temperature and decreases depending on curing time $\tau$. 
Figure 7. Dependence of $H - H_0$ from $T$ of water-1-propanol mixture ($x = 0.5$ mol. fraction) for different periods of time: 1 – in the beginning; 2–6 – after 1,2,3,4,5 hours respectively.

Figure 8. Dependence of $F - F_0$ from $T$ of water-1-propanol mixture ($x = 0.5$ mol. fraction) for different periods of time: 1 – in the beginning; 2–6 – after 1,2,3,4,5 hours respectively.

Table 3. The values of pressure of water–1-propanol mixture ($x = 0.5$) change during 5 hours.

| Time, min | water–1-propanol, ($x = 0.5$) |
|-----------|-------------------------------|
| 0         | 9.461 11.478 13.31 15.184 17.114 |
| 60        | 9.482 11.534 13.47 15.574 18.094 |
| 120       | 9.503 11.59 13.63 15.964 19.074 |
| 180       | 9.524 11.646 13.79 16.354 20.054 |
| 240       | 9.545 11.702 13.95 16.744 21.034 |
| 300       | 9.566 11.758 14.11 17.134 22.014 |

References
[1] Vukalovich M, Babikov Y and Rasskazov D 1970 Teplovizicheskiye svoystva organicheskikh teplonositeley (Moscow: Atomizdat)
[2] Chechetkin A 1971 Visokotemperaturniye teplonositeli (Moscow: Energiya)
[3] Babikov Y and Rasskazov D 1985 Organicheskiye i kremniiorganicheskiye teplonositeli (Moscow: Energoatomizdat)
[4] Rasskazov D, Babikov Y and Petrov E 1970 Trudi MEI 75 33–35
[5] Skorokhodov I 1972 Issledovaniye termicheskoy stabilnosti kremniyorganicheskikh soedineniy. - Khimiya I tehnologiya elementoorganicheskikh soedineniy. Kremniiorganicheskiye soedineniya (Moscow: NIITEKHM)
[6] Kosmulski M, Gustafsson J and Rosenholm J B 2004 Thermochimica Acta 412 47–53
[7] Baitalow F, Wolf G, Grolier J P, Dan F and Randzio S 2006 Thermochimica Acta 445 121–125
[8] Feron D and Lambert I 1992 Journal of Solution Chemistry 21 919–932
[9] Sobolevskiy M, Zhigalin G and Runzynaeva V 1972 Khimicheskaya promishlennost 7 494–496
[10] Rasskazov D, Babikov Y and Khamann K 1964 Teploenergetika 9 71–73
[11] Rasskazov D, Babikov Y and Belinskaya N 1965 Teploenergetika 8 83–84
[12] Debbade A 1963 Physical properties of organic coolants (England: Atomic Energy Establishment)
[13] Babikov Y, Buntushkin V and Gavrilin A 1982 Tr. MEI. 588 3–10
[14] Blake E, Hamma W, Edwards J, Reichard T and Ort M 1961 J. of Chem. Eng. Data 6 87–98
[15] Angelino G and Invernizzi C 2003 International Journal of Refrigeration 26 51–58
[16] Calderazzi L and di Paliano P 1997 International Journal of Refrigeration 20 381–389
[17] Johns B, McElhill E and Smith J 1968 IEC PRODUCT RESEARCH AND DEVELOPMENT 1 2–6
[18] Fabuss M, Borsanyi A, Fabuss B and Smith J 1963 Journal of Chemical and Engineering Data 6 64–69
[19] Invernizzi C, Iora P, Manzolini G and Lasala S 2017 Applied Thermal Engineering 121 172–179
[20] Ginosar D, Petkovic L and Guillon D 2011 Energy and Fuels 25 4138–4144
[21] Dzhapparov T and Bazaev A 2012 Teplofizika i aeromechanika 19 793–798
[22] Dzhapparov T and Bazaev A 2012 Journal of Materials Science and Engineering A 12 786–790
[23] Bazaev A, Abdulagatov I, Magee J, Bazaev E, Ramazanova A and Abdurashidova A 2004 Journal of Thermophysics 25 805–838
[24] Abdurashidova A, Bazaev A and Abdulagatov I 2007 High Temperature 45 178–186
[25] Kalafati D, Rasskazov D and Petrov E 1967 Teploenergetika 14 77–84
[26] Straty G, Palavra A and Bruno T 1986 Int. J. of Thermophysics 5 1077–1089
[27] Bazaev E and Bazaev A 2013 Russian Journal of Physical Chemistry A 87 925–955
[28] Gude M and Teja A 1995 J. Chem. Eng. Data 40 1025–1036
[29] Walas S 1985 Phase equilibria in chemical engineering (London: Butterworth Publishers)
[30] Shpilrayn E and Kesselman P 1977 Osnovi teorii teplofizicheskikh svoystv veshestv (Moscow: Energiya)