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EVAPORATION ANALOGIES BETWEEN LIGHT HYDROCARBONS

Effect of molecular mass of purge gas

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Abstract

The evaporation of benzene, cyclohexane, *n*-heptane, toluene, 2-xylene, 3-xylene and 4-xylene was studied in H_2, He, N_2 or CO_2 as purge gases for control of the introduced methods of evaluation and the sensitivity limits of TG measurements. I_i as a function of $(1-\alpha)$ and the following equation proved very suitable for a quantitative comparison of 28 independent and different TG measurements and for a very sensitive characterization of the thermal processes, even within an energy level difference of 3 kJ mol^{-1}, in spite of the known great inconsistency in the formal kinetic parameters:

$$\ln A \cong \overline{(1/RT_i)}\,\bar{E}_i - n\overline{\ln(1-\alpha)_i} + \overline{\ln(\mathrm{d}\alpha/\mathrm{d}t)_i}$$

The purge gases definitely influence the evaporation. The influence on the average vapour pressure is an exponential function of the product of the molecular mass and the boiling temperature.

With regard to the number of factors in the TG measurement. and the great sensitivity of I_i and the above function, it can be supposed that these equations exhibit some multivariate regression character, besides their natural parameter content.

The evaluation methods introduced help to extend the application of TG.

Keywords: dimensionless product, evaluation, evaporation, hydrocarbons, purge gases, TG

Introduction

The chemical characterization of examined substances remains the chief area of application of thermogravimetry (TG), though the importance of examinations of physicochemical properties of substances and measurements relating to thermodynamic processes (e.g. evaporation, grinding, etc) is increasing.

One indisputable result is the extension of gravimetric knowledge relating to the wide-ranging TG research and evaluation efforts, but the great inconsistencies in the formal kinetic parameters are also well known. On the other hand, it has been emphasized that the kinetic parameters correlate with each other strictly linearly as a manifestation of the so-called kinetic compensation effect (CE; $\ln A = aE \pm b$). Such experience has become the rightful source of the frequent critical, moreover, ironical

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remarks relating to TG mea-suring conditions and kinetic evaluation [1, 2]. The interpretation of the CE has been the subject of numerous considerations, among others as a consequence of different errors in the measured and calculated data.

The cause of the contradictions is concealed beneath the usual idea of looking for kinetic parameters which characterize the examined substance in a constant manner, for example according to Eq. (1):

$$\frac{d\alpha}{dt}=A\exp\frac{E}{RT}(1-\alpha)^{n} \qquad (1)$$

where $d\alpha/dt$ is the velocity of the thermal process, $(1-\alpha)$ is the fraction of unereacted substance, A is the pre-exponential factor, R is the universal gas constant, E is the activation energy, T is the absolute temperature, and n is the order of reaction.

It is a conceptual mistake, however, to calculate kinetic parameters to characterize a substance on the basis of one of its chemical reactions which depend on the process conditions. This idea supposes that only the activation energy of the 'pure', i.e. the 'abstract' chemical reaction is exponentially related to the process, and therefore the character of its description differs from the other partial processes (different form of diffusion, heat conduction, etc.) that are superimposed, but in an inseparable manner [1–5].

In spite of the usual kinetic evaluation idea as a principle or conceptual type of error, the analogy between the mass, energy, momentum streams and transport processes, and consequently between their exponential energy relations, is a proved fact in thermodynamics. This problem was solved by introducing Eqs (2) and (3), which preserve the structure of Eq. (1) to some degree, but which contain only series of sets of measured discrete values of the T, TG and DTG functions [3, 4]. I_i is reminiscent of the word invariant and Eq. (2) serves as its definition function:

$$I_i=\frac{E_i}{RT_i} \qquad (2)$$

$$\frac{E_i}{RT_i}=\ln\left[A\frac{(1-\alpha)_i^{n}}{\left(\frac{d\alpha}{dt}\right)_i}\right] \qquad (3)$$

Equation (3), as dimensionless group of numbers, illustrates the simple connections between the measured data. The simplifications that $A=1$ and $n=1$ are the basic presumptions for elimination from the usual preconceptions, e.g. relating to the rate-controlling processes. I_i, as a function of $(1-\alpha)_i$ and $1/T_i$, is very suitable for a quantitative comparison of the TG data measured under very different conditions by calculating the changes in A, n and the difference between the $1/T$ values in respect of the base. Accordingly, it can serve for a deeper and even quantitative investigation of some factors of measurements that are now included in the systematic error category (e.g. the mass and physical properties of the sample, the heating rate, etc.) [3–7].

In strict connection with the analysis of TG measurements with dimensionless product, Eq. (4) is suitable for an unambiguous, accurate and very sensitive characterization of different TG processes, using the measured data directly [4–7]:

$$\ln A \cong \overline{(1/RT_i)}\,\overline{E}_i - \overline{n\ln(1-\alpha)_i} + \overline{\ln(\mathrm{d}\alpha/\mathrm{d}t)_i} \qquad (4)$$

Equation (4) is in connection with the phenomenon of the CE, too but in contrast with the known idea of CE, the factors of Eq. (4) have direct and characteristic physical meaning: $\overline{(1/RT_i)}$ shows the average temperature dependence of the thermal process and the sum of the terms $\overline{-n\ln(1-\alpha)_i+\ln(\mathrm{d}\alpha/\mathrm{d}t)_i}$ points in a complex manner to the effects of the concentration and the structure of the sample and to the velocity of the process. In spite of the identical dimensions, the meaning of $\overline{E}_i$ differs fundamentally from the idea of the activation energy in the Arrhenius equation because $\overline{E}_i$ characterizes not merely the examined substance, but the energy level of the chemical reaction and the partial processes together [4, 5].

These results are proved and verified by analysis and comparison of the error levels of different types of evaluation methods and by recalculation of published data in the literature [4–7].

One rather neglected subject is the quantitative investigation of the effects of purge gases on TG results, especially in the case of the evaporation of liquid hydrocarbons. The number of factors that affect the precision, accuracy and reproducibility of the experimental results in TG has been estimated as several dozens [e.g. 8–13]. Investigation of the evaporation of light hydrocarbons increases the numbers of known factors, and the mechanisms of superimposed evaporation and condensation are independent. It is hoped that this study will lead to a better understanding of the relations between the large number of factors and the significant parameters of the thermal processes.

In this paper, the extension of the applicability and the limits of the quantitatively expressible sensitivity of TG measurements has been studied via Eqs (3) and (4), as recently introduced evaluation methods. Benzene, cyclohexane, *n*-heptane, toluene, 2-xylene, 3-xylene and 4-xylene were the substances examined, with regard to their molecular masses and boiling temperatures, with a standardized flow velocity of H_2, He, N_2 or CO_2 as purge gases.

Experimental procedures

The TG instrument used was the simultaneous (T, TG, DTG, DTA) thermobalance of Paulik, Paulik and Erdey (derivatograph) [9, 13]. The platinum sample holder had the shape of a hollow cylinder (visible in [1] Fig. 1 as the 2nd crucible). Its external and internal radii were 6.0 and 1.5 mm, respectively, and the height of the crucible was 16.0 mm. The separate bottom half of the inside cylinder contained the Pt–PtRh thermocouple. Its hot junction was at roughly the middle level of the liquid phase at the start of the measurements. The measured values were regarded as the 'temperature of the sample', though it is a known fact that there is a temperature distribution in the sample, and the sample quantity decreases continuously. The standardized heating rate was 1.3–1.4 K min^{-1}.

The sample quantity was 500±1.5 mg and the standard flow rates of the purging gases were 100±6 cm^3 min^{-1} for the different measurements. The gases were at atmospheric pressure.

Empirical experience

The TG curves revealed only a continuous mass decrease in each case during constant temperature increase. In most cases, the DTG curves also displayed a continuously changing character, but the DTA curves were always unexpectedly complex. The evaporation being an endothermic process, the double peak-like head sections of the DTA curves were as follows: decreasing, increasing constant-like section, decreasing. These sections more or less overlap in many cases. The heat conduction, the momentum stream, and the circulation in the liquid phase are factors relating to the mechanism of the process that are well observable in the DTA data in particular, and more seldom in the DTG data. Examples are shown in Figs 1 and 2. Figure 1 shows the complex system of the DTA sections and their dependence on the velocity of the purge gas. As concerns the effect of the velocity of the purge gas, 6.3, 4.4 and 3.5 were the average ΔK values for toluene at 105, 163 and 188 cm^3 min^{-1} He, respectively. The purges of this can be considered an encouraging result as regards the aim of this examination. Figure 2 depicts relatively rarely observed heterogeneous change in a DTG curve.

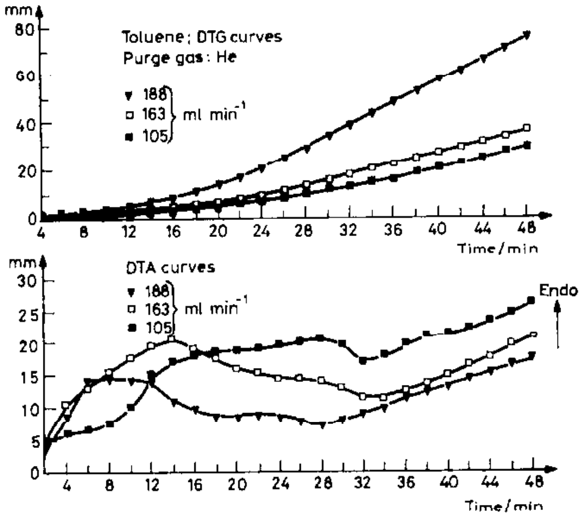

Fig. 1 Toluene; DTG and DTA curves as function of the flow rate of He purge gas

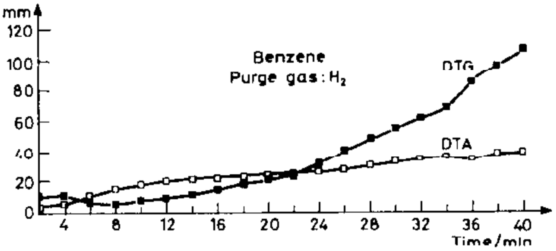

Fig. 2 Benzene; DTG and DTA curves. Purge gas: H_2

Analysis of DTA results

The thermobalance used furnishes a very simple tool for a quantitative comparison of the DTA curves. It is easy to measure in parallel the temperature of the sample and the sphere of heating for calculation of their differences and averages directly.

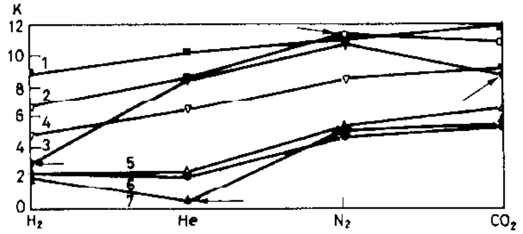

Fig. 3 Averages of ΔT sample and inert temperature during the thermal processes

These average results are shown in Fig. 3 as a pre-observation of the trends. The data prove that the averages of the temperature differences are connected with the molecular masses of the examined samples and the molecular masses of the purge gases.

The connections, however, are sensitive to the conditions of the measurements. The 4 dubious data (cyclohexane in N_2, 4-xylene in He, and *n*-heptane in H_2 or in CO_2) point to some measurement factors that are as yet not clear. On the other hand, and with reference to the known problem of the comparability of different TG measurements, 4 dubious data among 28 seems a very favourable ratio.

Discussion and quantification of purge gas effects

According to the published results [3–7], Eq. (3) as a function of $1-\alpha$ or $1/T$ is very suitable for the comparison of TG data measured quantitatively under very different conditions. The functions I_i proved well transformable for a quantitative comparison of the measurements. Comparison of the present measurements, however, did not give applicable function-like results as concerns the effects of the purge gases because of the small differences between the TG data.

As the following evaluation approach, Eq. (4) proved very suitable for a quantitative characterization of the different thermal processes. It was expedient, by the calculation of $\overline{(1/RT_i)}$ and the sum of terms $\overline{-n\ln(1-\alpha)_i + \ln(d\alpha/dt)_i}$ (as $\overline{b_i}$ in Table 1),

Table 1 Results calculated with Eq. (4) in the interval $(1-\alpha)=0.8-0.2$

Sample	Purge gas	$\overline{E_i}$	$\overline{(1/RT_i)}$	$\overline{b_i}$	$\overline{A_i^*}$	$\overline{T_i}$/ °C	$\overline{p_i}$ torr
Benzene	H_2	17.91	0.3666	–6.5644	0.98855	55.1	324.9
	He	18.01	0.3694	–6.6544	0.98998	52.6	293.7
	N_2	19.30	0.3619	–6.9831	0.98715	58.3	371.0
	CO_2	18.93	0.3659	–6.9277	0.98832	55.7	327.0
Cyclohexane	H_2	17.54	0.3722	–6.5295	0.98999	50.1	267.1
	He	17.82	0.3693	–6.5822	0.98971	52.7	294.9
	N_2	19.14	0.3630	–6.9496	0.98709	58.4	357.0
	CO_2	19.24	0.3635	–6.9944	0.98618	57.9	343.8
n–Heptane	H_2	18.39	0.3654	–6.7207	0.98795	56.2	176.0
	He	18.21	0.3570	–6.4997	0.98727	63.9	236.3
	N_2	20.32	0.3555	–7.2220	0.98741	65.4	250.2
	CO_2	20.05	0.3538	7.0969	0.98742	67.0	266.0
Toluene	H_2	19.05	0.3516	–6.6972	0.98819	69.1	191.2
	He	19.42	0.3500	–6.7977	0.98792	70.6	202.4
	N_2	20.80	0.3410	–7.0927	0.98506	79.7	273.0
	CO_2	20.77	0.3419	–7.1010	0.98598	78.7	263.9
2–Xylene	H_2	20.57	0.3396	–6.9855	0.98770	81.2	96.5
	He	20.37	0.3340	–6.8037	0.98935	87.1	122.4
	N_2	21.58	0.3265	–7.0455	0.98683	95.4	167.8
	CO_2	21.64	0.3300	–7.1425	0.98646	91.4	144.4
3–Xylene	H_2	20.29	0.3372	–6.8408	0.98955	83.7	127.6
	He	20.46	0.3351	–6.8577	0.99013	85.9	139.3
	N_2	21.46	0.3313	–7.1100	0.98646	90.0	163.1
	CO_2	21.06	0.3375	–7.1083	0.98709	83.4	128.8
4–Xylene	H_2	20.44	0.3314	–6.7731	0.99014	89.9	161.5
	He	19.83	0.3404	–6.7504	0.98988	80.3	116.3
	N_2	21.32	0.3340	–7.1198	0.98671	87.2	146.3
	CO_2	21.27	0.3374	–7.1780	0.98543	83.4	127.8

to use about twenty sets with equal scales of the measured T_i, $(TG)_i$ and $(DTG)_i$ data directly. $\overline{E_i}$ was calculated with these averages, considering that A=1. In other words, $\overline{E_i}$ is the abscissa of the straight line according to Eq. (4) at ln A=0, $\overline{b_i}$ is the intercept at $\overline{E_i}$=0 and $\overline{(1/RT_i)}$ is the slope.

The average results of the measurements calculated within the interval (1–α)=0.8–0.2 are given in Table 1. The $\overline{A_i^*}$ are data recalculated from the averages of the individual E_i, $(1/RT_i)$ and b_i results and it differs from '1' asymmetrically. The error is about 1.0–1.5%; referring to $\overline{E_i}$, the error is about 0.1–0.2% as some hidden reserve of the evaluation method used. Table 1 contains the average temperature and the connected average vapour pressure data.

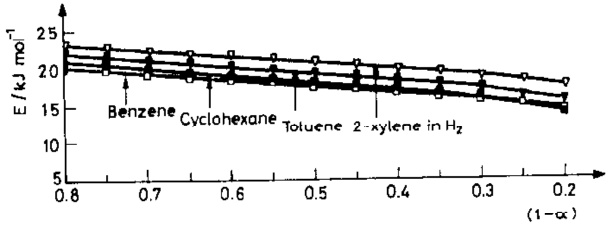

Fig. 4 Effect of hydrogen purge gas on evaporation

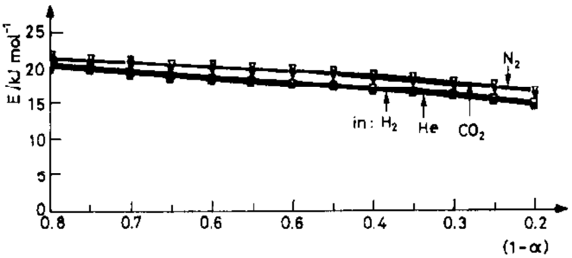

Fig. 5 Activation energy of evaporation of cyclohexane in different purge gases

As examples related to Table 1, Fig. 4 depicts some E *vs.* (1–α) functions for different hydrocarbons in H_2 atmosphere, and Fig. 5 the effects of different purge gases on cyclohexane.

The effects of the purge gases in Table 1 seem characteristic and distinguishable, but in spite of the direct comparison of the results, analysis of the differences of the functions was more expedient. The E *vs.* (1–α) functions measured in N_2 purge gas were chosen as the basis for the ΔE *vs.* (1–α) calculations.

According to the ΔE *vs.* (1–α) functions, H_2 with He and N_2 with CO_2 belong in different groups. This is illustrated in Fig. 6 with the cyclohexane results and in Fig. 7 with the *n*-heptane results as examples. The change in the rates of the partial processes during the thermal processes is noteworthy in these Figs too (e.g. in the vicinity of (1–α)≈0.5).

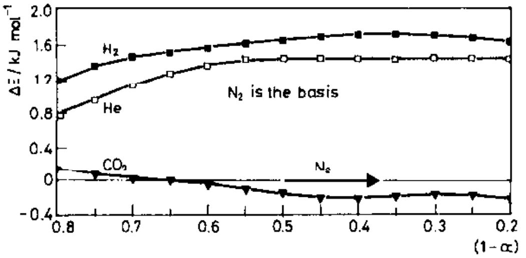

Fig. 6 Relative activation energy of evaporation of cyclohexane in different purge gases

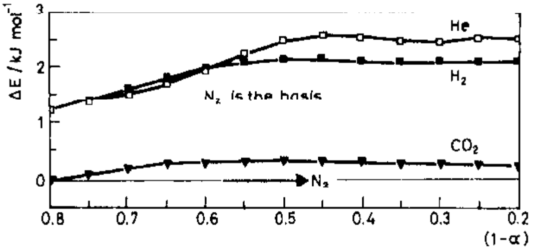

Fig. 7 Relative activation energy of evaporation of *n*-heptane in different purge gases

According to the empirical relation in Eq (5), it was found that y, the average vapour pressure, is an exponential function of the product x, which is the molecular mass multiplied by the boiling temperature ((molecular mass×boiling temperature)/1000):

$$y = ae^{bx} \tag{5}$$

The results of this relation are to be seen in Table 2, completed with averages of all pairs of y *vs.* x results, for $(1-\alpha)=0.5$ and the interval 0.8–0.2. The results allow a general survey of the effects of purge gases on the seven examined hydrocarbons in the interval $(1-\alpha)$–0.8–0.2.

Table 2 Effects of purge gases on evaporation of light hydrocarbons

	H_2	He	N_2	CO_2	$(1-\alpha)$	
					0.5	0.8–0.2
a	546.07	590.82	703.10	744.69	682.42	642.78
b	–0.100	–0.103	–0.100	–0.113	–0.104	–0.104
r	0.929	0.983	0.985	0.973	0.997	0.998

a and b are the constants in Eq. (5); r is the coefficient of linear regression

The effects of purge gases are within 3 kJ mol^{-1}, so Eqs (4) and (5) are suitable or a deep exploration of the mechanism of the effects.

The connection is difficult to understand because of the great sensitivity of the evaluation methods introduced, and the numerous factors involved in the TG measurements. For an explanation, it is obvious that the measured T_i, $(TG)_i$ and $(DTG)_i$ data contain the effects of all the measurement factors, but with a special hierarchy, so it must be supposed that these equations have some statistical, some multivariate regression character, too, besides their natural content. As an analogy, reference may be made to some results published earlier [2], i.e. the close connection between the coefficients of the sixth-order polynomials of the measured DTG curves as functions of sample quantity. In that case, the close connection of the statistical coefficients is reminiscent of the CE, as the phenomenon of the kinetic parameters.

Conclusions

The evaporation of light hydrocarbons in different purge gases was studied in order to control the introduced evaluation method and to extend the applicability of TG measurements.

It was demonstrated that the average I_i *vs.* $(1-\alpha)$ very sensitively characterizes the thermal processes, according to the following equation:

$$\ln A \cong \overline{(1/RT_i)}\ \overline{E_i} - \overline{n\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i}$$

The nature of the purge gas definitely influences the evaporation of the examined light hydrocarbons. The influence on the average vapour pressure proved to be an exponential function of the product of the molecular mass and the boiling temperature.

Though evaporation increases the number of factors involved in the measurements, I_i as a function of $(1-\alpha)$ was very suitable for quantitative comparison of the different TG data in the case of 28 independent measurements, even within an energy level difference of 3 kJ mol^{-1}, in spite of the known considerable inconsistency of formal kinetic parameters.

With regard to the number of factors in the TG measurements and the great sensitivity of the introduced functions, it can be supposed that these equations have some multivariate regression character, besides their natural content.

These evaluation methods help broaden the application of TG, with an extension of the idea of 'measured factors' to the detriment of 'disturbing factors' or 'source of errors'.

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