Characterization of Hydrocarbon Systems by DBE Concept

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Thermochemical data of mineral oil fractions are scarce. Due to the complex structure of natural hydrocarbon mixtures, standard heat and Gibbs free energy of formation depend on the sample. A procedure for predicting these properties is presented. Both properties depend on the hydrocarbon type and on its molecular weight. The double-bond equivalent (DBE) and the number of olefinic double bonds are the important characterization parameters of the model. DBE can basically be calculated from molecular weight and elemental composition. Alternatively, boiling point and atomic H/C ratio can be used if the model is applied to mineral oil fractions from which boiling curves can be obtained. A criterion for testing the reliability of the estimated DBE value is available, because DBE is also a function of structural group distribution.

The relevance of the DBE concept is shown with regard to hydroprocessing of mineral oil fractions. The model can be applied to total average molecules as well as to an arbitrary number of pseudocomponents and continuous mixtures. The difference between feed and product DBE is equivalent to the amount of hydrogen consumed for hydrogenation of unsaturated hydrocarbons. Further properties of the product can be predicted.

Introduction

For process simulation of chemical reactors and complete plants it is vitally important to have reliable procedures for estimating physical, chemical, and thermochemical properties. Very suitable methods and databases are available, for example, in Reid et al. (1987), when the composition of feedstock and products, and the chemical reactions that are involved are known.

In the petroleum industry complex hydrocarbon mixtures are involved where the number of components increases when the boiling range of the fractions rises. This causes a drastic fall in the degree of analytical identification. A complete analysis of crude oils has not been successful until now. The theoretically possible number of paraffin isomers gives an idea of this problem: 75 isomers with 10 carbon atoms can exist, so at a carbon number of 20 we may find about 366,000 paraffin isomers, while if the carbon number is 100, the probability of finding a specific isomer increases to $1{:}5.92\times10^{39}$ (Altgelt and Boduszynski, 1994).

In order to calculate the properties of liquid mineral-oil fractions, which are mixtures of unknown composition, adequate lumping and characterization procedures are required. In this way a whole fraction of numberless (not infinite) components can be defined as a single, average component. If different feedstocks are mixed, or if vapor–liquid equilibrium calculations have to be performed, breaking the original average fractions down into a number of pseudocomponents improves the accuracy of the predictions. Every pseudocomponent represents a lump of numerous hydrocarbons, and each lumped group has to be characterized in a suitable way.

The properties that are important for process simulations, such as density, viscosity, and heat capacity, are measured characteristics of the total fraction. In order to predict properties of the average oil from simple measures, empirical factors have been defined that should reflect the characteristic behavior of the fraction without having any fundamental physical or chemical meaning. These characterization factors are calculated from the physical properties of the total sample. The most widely known number in the petroleum industry is the Watson Characterization Factor (Watson and Nelson, 1933). Watson and Nelson noted that the Characterization Factor calculated as the ratio of the cube root of the absolute boiling point (in °R) to the specific gravity would be mainly constant for the paraffin hydrocarbons that boil between 38°C and 371°C, if the averages of all the reported isomers are considered. This cannot be confirmed by the experimental data available today, as is shown in Figure 1. Ap-

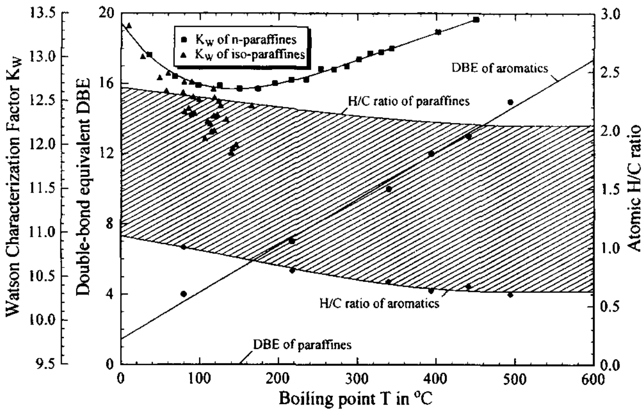

Figure 1. Characterization of mineral-oil fractions.

plication of empirical characterization factors is limited to fractions, from which the required analytical data, especially the boiling curve, can be obtained.

A characterization procedure is described in this article, which takes into account the different behavior of the hydrocarbon classes. The double-bond equivalent (DBE), which is used as a characterization factor, can basically be calculated from the molecular weight and elemental composition of the sample or from structural group analytical data. This makes it possible to apply the correlations even to nonboiling hydrocarbons, such as vacuum residues. Distillates are usually characterized by their boiling curve and specific gravity. When using these data we can estimate the molecular weight by means of empirical correlations, should no experimental value be available.

Riazi and Daubert (1987) have shown that the average and the maximum errors in the prediction of molecular weight by the procedure of Winn (1957), Kesler and Lee (1976), and Twu (1984) are on the order of 6% and 25%, respectively. The average and maximum error of their new correlation have been given as 2.2% and 18.7%. The equation published by Sim and Daubert (1980) is based on the graphical procedure by Winn (1957). The same type of equation for predicting molecular weight from a given boiling point and specific gravity is used by Riazi and Daubert (1980a). On the basis of a data set that was larger than the one used in 1957, Riazi and Daubert (1980a) got different coefficients from those found by Sim and Daubert (1980). Trytten and Gray (1990) noted that molecular-weight data estimated by using the method by Sim and Daubert (1980) are at least 10% higher than measured values. Their feedstocks were narrow-boiling fractions of syncrude coker gas oil, characterized by their large specific gravities and high content of aromatic carbon atoms. Riazi and Al-Sahhaf (1995) recently published a correlation that describes the intercorrelation between molecular weight and boiling point of some homologous series of hydrocarbons. The type of equation implies that each homologous series has a characteristic limiting boiling point for an infinite number of carbon atoms.

In this article the fundamental interconnection between molecular weight, the atomic H/C ratio, the number of carbon atoms, and the DBE is discussed and the relevant correlations are given. In accordance with the model by Riazi and Al-Sahhaf (1995) defined interconnections exist between several properties within each homologous series. The DBE concept is developed on the basis of pure hydrocarbons, and its application to pseudocomponents and to total average fractions is demonstrated.

The heat of reaction is very important in performing reactor heat balances. As long as the reactions and the components are well-defined, the standard heat of reaction can be calculated from the standard heats of formation of all the components involved in the reaction. Standard heat-of-formation data of many pure components can be found in databases, for example, in Reid et al. (1987) or in Perry and Green (1984). If the standard heat of formation of a known component cannot be found, its value can be approximated by a group-contribution method (Reid et al., 1987).

If reactors for hydrotreating or hydrocracking of mineral oil fractions are simulated, the problem of predicting the heat of reaction becomes obvious. The typical, average values assigned to the heat of reaction of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodearomatization (HDA), and hydrocracking can be found in the literature (Döhler and Rupp, 1987; Mohanty et al., 1991a,b). Jaffe (1974) gives an overview concerning the heats of reaction of many different pure-component hydrogenation reactions that may be applied to multicomponent feedstocks of similar structure.

Edmister (1988) has published an equation from which the heat of reaction of ten endothermic petroleum refining processes can be estimated. Molecular weight of the feed and product as well as a constant that is a characteristic of each process, are the parameters of Edmister's correlation. Montgomery (1988) presents a method for predicting the standard heat and free energy of formation. The model requires reliable quantitative analysis concerning the distribution into paraffinic, naphthenic, and aromatic components, whereas olefins have been neglected. The heavier the fraction, the greater the uncertainty of the required analysis. The presence of aromatic–naphthenic components as well as the choice of the analytical separation process and detector are further sources of uncertainty.

A new procedure that can predict standard heat-of-formation data of mineral oil fractions and their pseudocomponents is presented here. The overall heat of reaction can be estimated based on these heats of formation.

After analyzing the hydrogenation of the pure aromatic components, it is obvious that the hydrodearomatization reactions are equilibrium reactions (Frye, 1962; Frye and Weitkamp, 1969). Döhler and Rupp (1987), Yui and Sanford (1991), and Korsten and Hoffmann (1996) show that the HDA of industrial feedstock is also affected by chemical equilibrium.

In order to predict the chemical equilibrium constant, standard Gibbs free energy-of-formation data of the components are required, from which the standard free energy of reaction can be calculated. Even equilibrium constants of well-defined pure-component hydrogenations are difficult to predict, because only few energy-of-formation data are available in the literature. In this article a new procedure for predicting standard free energy of formation is presented. This procedure can be applied to hydrocarbon mixtures and their pseudocomponents.

The DBE-concept shows good agreement between calculated properties and data published in the literature.

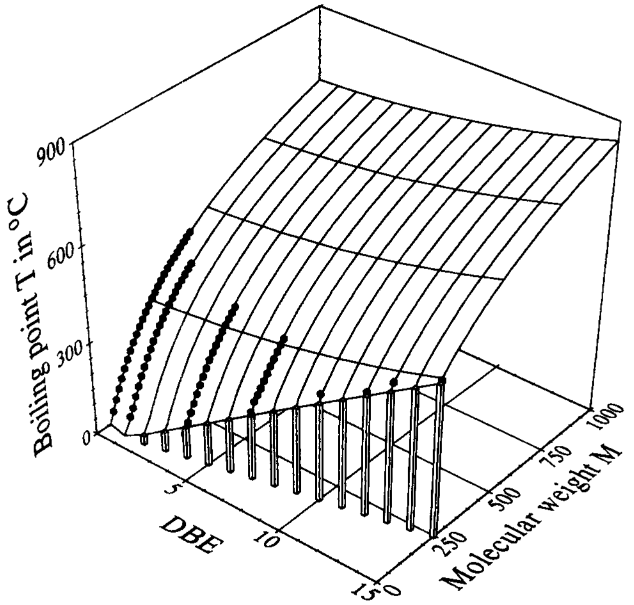

Figure 2. Hydrocarbon characterization chart.

Boiling Point and Molecular Weight of Pure Hydrocarbons

Our intention is to make procedures available that can be used to predict the important properties of undefined hydrocarbon mixtures from properties that can easily be measured. In order to allow wide extrapolation with minimum risk of misprediction, empiricism should be reduced to a minimum. The fundamental basis of the characterization procedure is shown in Figure 2. Neglecting the group of isoparaffins, which have boiling points that are on average 12.4°C below the corresponding n-paraffins, it is obvious that all hydrocarbons are within the two borders represented by the n-paraffins and the condensed-ring aromatics. The data of the n-paraffins up to C_{30} and the other hydrocarbons are taken from the API Handbook (1994). The boiling temperature T_P in °C of the n-paraffins is calculated from the number of C atoms, n, by means of the correlation published by Glinzer (1985):

$$T_P = 266.5 \cdot \ln n - 456.5 - 217.37 \cdot F\left(-\frac{n}{6}\right), \tag{1}$$

where $F(-n/6)$ is the integral-exponential function:

$$F\left(-\frac{n}{6}\right) = \int_{-\infty}^{-n/6} e^x \, d(\ln x). \tag{2}$$

Integration of Eq. 2 delivers

$$F\left(-\frac{n}{6}\right) = C_E + \ln\left|-\frac{n}{6}\right| + \sum_{k=1}^{\infty} \frac{\left(-\frac{n}{6}\right)^k}{k \cdot k!}, \tag{3}$$

where C_E is the Euler constant ($C_E = 0.577216$). Equation 3 decreases very rapidly with increasing C number n, so that the last term in Eq. 1 can be neglected if $n \geq 25$. For $n \geq 5$, the boiling points calculated by Eq. 1 are with an average deviation of 0.18°C and a maximum error of 0.60°C, which is almost identical to the experimental data given in the API Handbook (1994).

Characterization of Hydrocarbons by DBE

All types of hydrocarbons can be described by the structural formula:

$$C_n \, H_{2n+z}, \tag{4}$$

where z is the hydrogen deficiency. The DBE is defined as follows:

$$\text{DBE} = 1 - \frac{z}{2}. \tag{5}$$

Model development

All paraffins are characterized by DBE = 0. As is obvious from Figure 2, the boiling points of all the homologous series along the molecular weight are parallel. In the DBE characterization procedure the boiling-point curve of the n-paraffines is chosen as a reference, and the boiling point T of any other hydrocarbon is calculated by means of the excess temperature T_E:

$$T = T_P + T_E, \tag{6}$$

where T_P is the boiling point of the n-paraffine with the same C number. The excess temperature can be calculated by the equation

$$T_E = (2.450 \cdot \text{DBE} + 0.53163 \cdot \text{DBE}^2) \cdot \Theta_T \tag{7}$$

with the parameter

$$\Theta_T = \frac{\text{DBE} - 2 \cdot \text{DB}_\text{O}}{|\text{DBE} - 2 \cdot \text{DB}_\text{O}|}, \tag{8}$$

where DB_O is the number of olefinic double bonds. The average deviation of the 115 data sets investigated is 4.1°C, and the maximum deviation is 9.8°C. The curves shown in Figure 2 have been obtained from Eq. 7. If the fraction of aromatic carbon atoms is known, it is possible to improve the prediction further by using Eq. 9:

$$T_E = (0.86681 \cdot \Theta_\text{A} + 0.105935 \cdot \Theta_\text{A}^2) \cdot \Theta_T, \tag{9}$$

with the structural parameter Θ_A:

$$\Theta_\text{A} = 5 \cdot \text{R} + \text{DB}_\text{R} + 2 \cdot \text{DB}_\text{O} \tag{10}$$

where R represents the number of rings and DB_R is the number of double bonds in the rings. The average deviation from experimental data is decreased to 2.1°C, and the maximum deviation is slightly increased to 11.8°C.

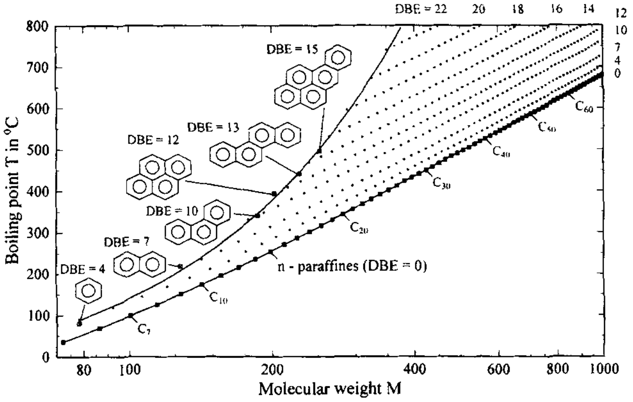

Figure 3. Importance of DBE in hydrocarbon characterization (cf. Severin, 1991).

The molecular weight of hydrocarbons can be calculated as

$$M = n \cdot M_C + 2 \cdot (n + 1 - \mathrm{DBE}) \cdot M_H, \tag{11}$$

where M_C and M_H are the molecular weight of carbon and hydrogen, respectively. Pedersen et al. (1989) proposed the following expression for estimating the molecular weight of high-boiling hydrocarbon fractions:

$$M = 14 \cdot n - 4, \tag{12}$$

which represents a simplification of Eq. 11 for the case DBE ≈ 3.

Figure 3 contains lines of constant DBE that are graphically represented by dots for each even number of C atoms. Following the recommendation by Severin (1991), the diagram contains the boiling point and the logarithmic representation of molecular weight. It is obvious from Figures 1 and 3 that the range of DBE values rises with increasing boiling range; this reflects the fact that the probability of finding highly condensed aromatic components increases with higher boiling points. The lines of a constant H/C ratio are shown in Figure 4. In contrast to DBE, the H/C ratio is not generally constant within every class of hydrocarbon, as is shown in Table 1. From Eq. 4 it is obvious that the limiting H/C value of all hydrocarbons is H/C = 2 for an infinite number of carbon atoms. From this limiting startpoint the H/C ratio increases with a reduced number of carbon atoms for $z > 0$, whereas it decreases for $z < 0$. Since DBE is correlated with the H/C ratio by Eq. 13,

$$\mathrm{DBE} = 1 - \left(\frac{\mathrm{H/C}}{2} - 1 \right) \cdot n, \tag{13}$$

it is possible to use any two of the parameters T, M, H/C, DBE, n together with the olefin content in order to estimate the remaining values.

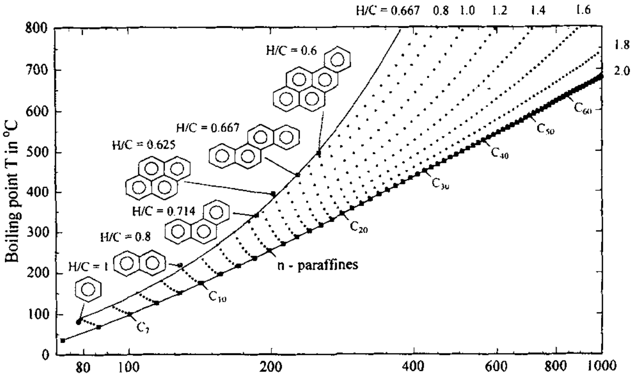

Figure 4. Atomic H/C ratio as characterization parameter.

Table 1. Characteristics of Homologous Series of Hydrocarbons

Hydrocarbon	General Formula	DBE	H/C	DB_O	R	DB_R
Paraffines	C_nH_{2n+2}	0	$2 < \mathrm{H/C} \leq 4$	0	0	0
Alkyl-cycloparaffines	C_nH_{2n}	1	2	0	1	0
Monoolefins	C_nH_{2n}	1	2	1	0	0
Diolefins	C_nH_{2n-2}	2	$4/3 \leq \mathrm{H/C} < 2$	2	0	0
Alkylbenzenes	C_nH_{2n-6}	4	$1 \leq \mathrm{H/C} < 2$	0	1	3
Alkylnaphthalenes	C_nH_{2n-12}	7	$0.8 \leq \mathrm{H/C} < 2$	0	2	5

Effect of heteroatoms

The structural formula, Eq. 4, does not contain heteroatoms like sulfur, nitrogen, and oxygen. In fact, the boiling points of hydrocarbons containing heteroatoms are different from those of pure hydrocarbons with the same molecular weight and DBE, as comparison between mercaptans and paraffines shows; both have the value DBE = 0. The chemical structure of a heteroatom containing a hydrocarbon is

$$C_nH_{2n+z}S_uN_vO_w. \tag{14}$$

A pure hydrocarbon must have the same molecular weight to transform this formula into a pseudohydrocarbon with the structure of Eq. 4, which allows us to define the pseudo-DBE_m as

$$\mathrm{DBE}_m = \mathrm{DBE} + u \cdot \frac{M_S}{M_C} + v \cdot \frac{M_N}{M_C} + w \cdot \frac{M_O}{M_C}. \tag{15}$$

The corresponding boiling temperature of the n-paraffine has to be calculated by using the modified carbon number n_m of the pseudomolecule:

$$n_m = n + u \cdot \frac{M_S}{M_C} + v \cdot \frac{M_N}{M_C} + w \cdot \frac{M_O}{M_C}. \tag{16}$$

Interconnection Between DBE and Structural Group Analysis

As recently noted by Altgelt and Boduszynski (1994), the hydrogen deficiency z can be calculated from the number of rings, R, and the number of double bonds, DB:

$$z = -2 \cdot (\mathrm{R} + \mathrm{DB} - 1). \tag{17}$$

Comparison with Eq. 5 shows that

$$\mathrm{DBE} = \mathrm{R_N} + (\mathrm{R_A} + \mathrm{DB_R}) + \mathrm{DB_O}, \tag{18}$$

where R_N and R_A represent the number of naphthenic and aromatic rings, respectively, and DB_R and DB_O are the number of double bonds within a ring or an olefin.

As shown in Table 1, both ways for calculating DBE—by Eqs. 4 and 5 (heterocomponents by Eqs. 5 and 14) and by Eq. 18—give the same results. This equality can be used as a criterion for determining whether the calculated DBE value of a mineral-oil fraction of unknown compositon is reliable or not.

Indirect structural group analysis

Several methods have been developed that promise to predict the percentage of paraffinic, naphthenic, and aromatic carbon atoms of mineral-oil fractions, the PNA-distribution (van Nes and van Westen, 1951; King et al., 1960; Riazi and Daubert, 1980b). Data that are necessary for predicting are usually the refractive index n_D, the specific gravity d, the molecular weight M, or the viscosity μ of the sample.

The specific gravity and the refractive index of a homologous series of hydrocarbons can be described by a correlation published by Smittenberg and Mulder (1948):

$$x = x_\infty + \frac{k_1}{M + k_2}, \tag{19}$$

where x represents the specific gravity or the refractive index, respectively, and x_∞ is the corresponding property of the hypothetic hydrocarbon with infinite molecular weight. These properties are shown in Figures 5 and 6 for several classes of hydrocarbons. The areas are calculated by means of Eq. 19, neglecting the constants k_2. The coefficients k_1 are functions of DBE.

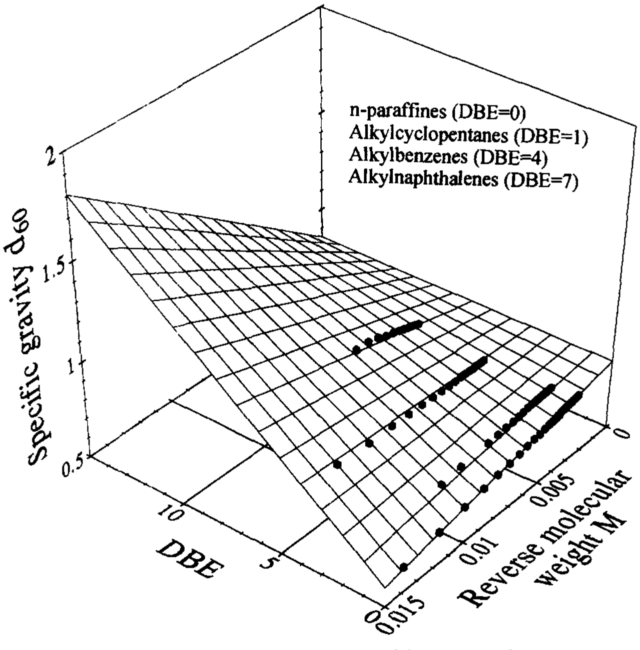

Figure 5. Specific gravity of hydrocarbons.

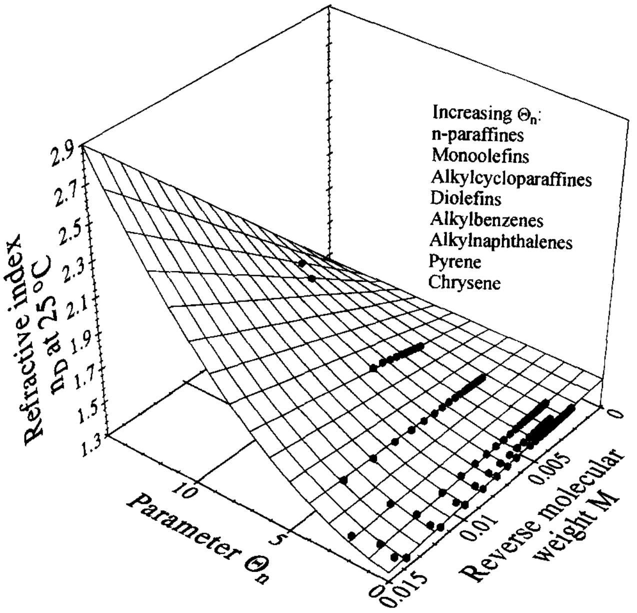

Figure 6. Refractive index of hydrocarbons.

The molecular weight, M, an important characteristic parameter of the DBE concept, is also one of the properties used in the *n-d-M* method by van Nes and van Westen (1951), which is given in Table 2.

Direct, analytical structural group analysis

There are several spectroscopical and chromatographical procedures available for determining the structural groups in mineral-oil fractions. These procedures give different types of information. Information is available from nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR) about the fraction of

Table 2. *n-d-M* Method at 20°C

Two parameters:
$a = 2.51 \cdot (n - 1.4750) - (d - 0.8510)$
$b = (d - 0.8510) - 1.11 \cdot (n - 1.4750)$

Fraction of aromatic carbon atoms:
$C_A = 4.30 \cdot a + 36.60/M \quad a > 0$
$C_A = 6.70 \cdot a + 36.60/M \quad a < 0$

Fraction of C-atoms in a ring:
$C_R = 8.20 \cdot b - 3 \cdot w_S^* + 100/M \quad b > 0$
$C_R = 14.40 \cdot b - 3 \cdot w_S + 106/M \quad b < 0$

Fraction of naphthenic carbon atoms:
$C_N = C_R - C_A$

Fraction of paraffinic C atoms:
$C_P = 1 - C_R$

Number of aromatic rings in the average molecule:
$R_A = 0.44 + 0.055 \cdot a \cdot M \quad a > 0$
$R_A = 0.44 + 0.080 \cdot a \cdot M \quad a < 0$

Total number of rings in the average molecule:
$R = 1.33 + 0.146 \cdot (b - 0.5 \cdot w_S) \cdot M \quad b > 0$
$R = 1.33 + 0.180 \cdot (b - 0.5 \cdot w_S) \cdot M \quad b < 0$

Number of naphthenic rings in the average molecule:
$R_N = R - R_A$

Source: van Nes and van Westen, 1951.
$^*w_S$ = weight fraction of sulfur.

Table 3. Estimation of Structural Data*

Number of aromatic rings in the average molecule:	
$\mathrm{R_A} = \dfrac{n_\mathrm{A} - 2}{4}$	$\mathrm{R_A} \geq 1$
$\mathrm{R_A} = \dfrac{n_\mathrm{A}}{6}$	$\mathrm{R_A} \leq 1$
Number of paraffinic C-atoms:	
$n_\mathrm{P} = \dfrac{m_\mathrm{P} - 1}{2}$	$\mathrm{DBE} > 0$
$n_\mathrm{P} = \dfrac{m_\mathrm{P} - 2}{2}$	$\mathrm{DBE} = 0$
Number of naphthenic C-atoms:	
$n_\mathrm{N} = n - n_\mathrm{P} - n_\mathrm{A} - n_\mathrm{O}$	
Number of naphthenic rings in the average molecule:	
$\mathrm{R_N} = \dfrac{n_N + 2 \cdot \mathrm{R_A} - 2}{4}$	$\mathrm{R} \geq 1$ and $\mathrm{R_A} \leq 1$
$\mathrm{R_N} = \dfrac{n_\mathrm{N}}{4}$	$\mathrm{R} \geq 1$ and $\mathrm{R_A} \geq 1$
$\mathrm{R_N} = \dfrac{n_\mathrm{N}}{6}$	$\mathrm{R} \leq 1$
Number of double bonds in the rings:	
$\mathrm{DB_R} = 3 \cdot \mathrm{R_A} - (\mathrm{R_A} - 1)$	$\mathrm{R_A} \geq 1$
$\mathrm{DB_R} = 3 \cdot \mathrm{R_A}$	$\mathrm{R_A} \leq 1$

*n_i = number of C-atoms in structure i; m_i = number of H-atoms in structure i.

Table 4. Specification of Vacuum Gas Oil

True boiling points:	
IBP	246°C
5 vol. %	319°C
10 vol. %	354°C
20 vol. %	421°C
30 vol. %	466°C
40 vol. %	498°C
50 vol. %	524°C
60 vol. %	537°C
70 vol. %	551°C
80 vol. %	566°C
90 vol. %	583°C
95 vol. %	594°C
FBP	615°C
Average true boiling point	491°C
Molecular weight (VPO)	420
Refractive index (20°C)	1.5128
Specific gravity (20°C)	0.9130
Specific gravity (15.6°C)	0.9155
Elemental composition:	
C	85.94 wt. %
H	12.18 wt. %
S	2.00 wt. %
N	1345 wppm
Fraction of aromatic C atoms (NMR)	22.4%

H and C atoms in typical structures, whereas liquid chromatography (LC) or thin-layer chromatography (TLC/FID) separates into classes of typical components.

Using Eq. 18 to estimate DBE from chromatographic structural group analysis is possible if the amount of aromatic and naphthenic rings is known. Even if a reliable separation into classes of different ring numbers, both for the aromatic and the naphthenic components, is obtained, the required values are very uncertain, because information about paraffinic side chains is lacking. Further uncertainty of chromatographical results is caused by components containing aromatic and naphthenic rings.

The important data for calculating DBE from spectroscopical results can be obtained if we assume that:

1. Each complete ring has six C atoms.
2. Condensed rings have two common C atoms.
3. If an aromatic and a naphthenic ring are connected, the two common C atoms are defined as aromatic C atoms.
4. Paraffinic C atoms are in one side chain, which is connected to the naphthenic ring, if there is one. Otherwise it is connected to the aromatic ring.

Table 3 contains the equations for calculating the parameters that are necessary for estimating the DBE by means of Eq. 18. As an example, the experimental data are shown in Table 4, while Table 5 contains the characterization of the heavy VGO.

Thermochemical Properties

To perform heat balances of reacting systems, we must have information about the heat of reaction. If the reaction

$$\nu_1 A_1 + \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4 \qquad (20)$$

is going on, the heat of reaction at standard conditions (1 atm, 25°C, gas phase) can be calculated by the following equation:

$$\Delta_R H^0 = \sum_{i=1}^{N} \nu_i \cdot \Delta_f H_i^0, \qquad (21)$$

where ν_i and $\Delta_f H_i^0$ are the stoichiometric coefficient and the standard heat of formation of component A_i, respectively.

The chemical equilibrium of this reaction can be predicted if we know the Gibbs free energy of reaction at standard conditions, $\Delta_R G^0$. For estimation of $\Delta_R G^0$ information is re-

Table 5. Characterization of the VGO from Table 4

From molecular weight M and elemental composition:	
Number of C atoms, n	29.97
DBE	5.65
Number of C atoms in the pseudohydrocarbon, n_m	30.72
DBE_m of the pseudohydrocarbon	6.39
Boiling point of the corresponding *n*-paraffine, T_p	456°C
Excess temperature, T_E	37°C
Boiling point of the average VGO molecule, T	493°C
From *n-d-M* method (Table 2):	
Fraction of aromatic C atoms, $\mathrm{C_A}$	22.9%
Fraction of naphthenic C atoms, $\mathrm{C_N}$	11.3%
Fraction of aromatic C atoms, C_P	65.8%
Number of aromatic rings, $\mathrm{R_A}$	1.20
Number of naphthenic rings, $\mathrm{R_N}$	0.75
From procedures in Table 3:	
Number of aromatic rings, $\mathrm{R_A}$	1.22
Number of naphthenic rings, $\mathrm{R_N}$	0.96
Number of ring double bonds, $\mathrm{DB_R}$	3.44
DBE	5.62
Thermochemical data:	
Standard heat of formation, $\Delta_f H^0$	−315 kJ/mol
Standard free energy of formation, $\Delta_f G^0$	354 kJ/mol

quired about the stoichiometry and the standard Gibbs free energies of formation of the components, $\Delta_f G_i^0$:

$$\Delta_R G^0 = \sum_{i=1}^{N} \nu_i \cdot \Delta_f G_i^0. \tag{22}$$

The application of Eqs. 21 and 22 to the reactions, where hydrocarbon mixtures of unknown composition are involved, was limited by a lack of information about the stoichiometry and standard heat and energy of formation. These data can be estimated using the DBE concept.

Standard heat of formation

If data about the standard heat of formation of a well-defined component cannot be found, the value can be approximated by a group-contribution method, as described by Reid et al. (1987). The experimental pure-component data shown in Figure 7 are taken from Reid et al. (1987), Yaws and Chiang (1988), and from table 7H1.2 (1992) of the API Handbook (1994).

It is obvious from Figure 7 that the dependence of the standard heat of formation on molecular weight is identical for each class of hydrocarbons. Since the homologous series of hydrocarbons can be characterized by DBE and the number of olefinic double bonds, $\mathrm{DB_O}$, the heat of formation can be expressed by the straight-line equation:

$$\Delta_f H_i^0 = a_0(\mathrm{DBE}, \mathrm{DB_O}) - 1.47402 \cdot M_i. \tag{23}$$

As shown in Figure 8, the coefficient a_0 as characteristic of the hydrocarbon class is well-described by the following equation in order to deliver the standard heat of formation in kJ/mol:

$$a_0 = 1604.25 \cdot (1 - 1.02481 \cdot e^{-\Theta_H/27.587}), \tag{24}$$

where the parameter Θ_H is defined as

$$\Theta_H = \mathrm{DBE} + 1.13 \cdot \mathrm{DB_O^{1.524}} + (\Psi_S + \Psi_N + \Psi_O). \tag{25}$$

The parameters Ψ_i, reflecting the influence of sulfur, nitrogen and oxygen components on the heat of formation, can be estimated from the number of S, N, O atoms, n_i, in the molecule:

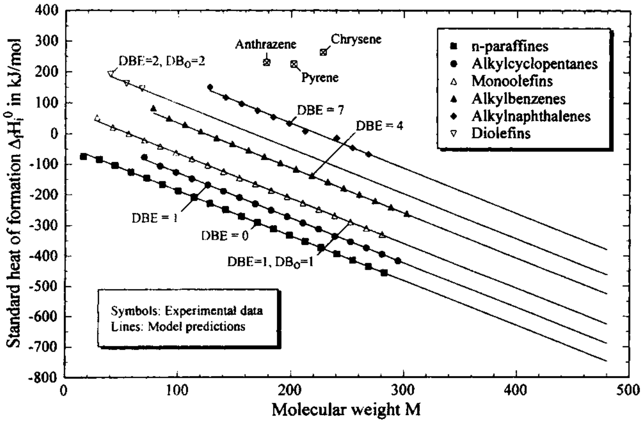

Figure 7. Prediction of standard heat of formation.

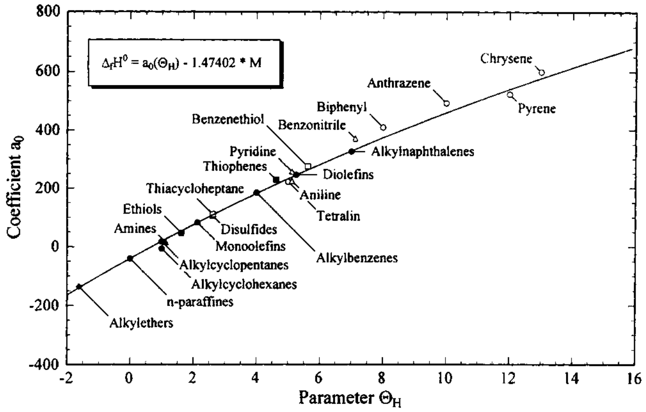

Figure 8. Impact of the hydrocarbon-type on heat of formation.

$$\Psi_i = (2 \cdot n_i)^{0.69}. \tag{26}$$

In Figure 8 the straight lines, which are in accordance with group contribution methods, are the result of the model prediction. The purpose of Eq. 26 is to predict heat-of-formation data of real hydrocarbon mixtures that also may contain heteroatoms. Information about the different isomeric structures, especially of the heterocomponents, is usually not available. The heat of reaction is calculated as the difference between the heat of formation of feedstock and product. If hydrogenation of undersaturated hydrocarbons is considered, the effect of isomeric structures can be neglected if the component remains in the same isomeric structure.

Standard Gibbs free energy of formation

The possibilities for predicting free energies of formation are similar to those of getting heat-of-formation data, discussed in the previous subsection. The standard Gibbs free energy of formation of each homologous series of hydrocarbons rises with increasing molecular weight, as shown in Figure 9. The pure-component data are taken from Reid et al. (1987) and from the API Handbook (1994). As in Eq. 23 the standard Gibbs free energy of formation in kJ/mol can be estimated by the following equation:

$$\Delta_f G_i^0 = b_0(\mathrm{DBE}, \mathrm{DB_O}) + 0.59501 \cdot M_i. \tag{27}$$

The characteristic parameter b_0 is correlated with DBE and the number of olefinic double bonds:

$$b_0 = 592.44 \cdot (1 - 1.0843 \cdot e^{-\Theta_G/20.661}), \tag{28}$$

where the parameter Θ_G is defined as follows:

$$\Theta_G = \mathrm{DBE} + 2.03 \cdot \mathrm{DB_O^{1.696}}. \tag{29}$$

Statistical data concerning the deviation of the predicted standard heat and free energy of formation from experimental data are given in Table 6.

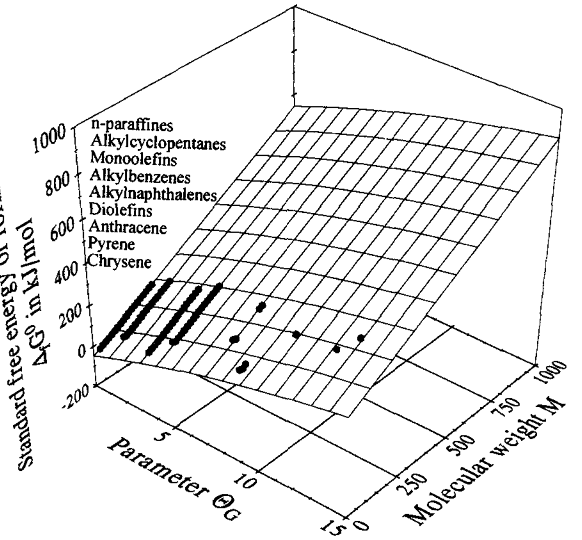

Figure 9. Prediction of standard Gibbs free energy of formation.

The procedure for predicting free energy of formation does not take into account heteroatoms. In hydrotreating mineral-oil fractions the reactions of heterocomponents with hydrogen, as well as hydrodearomatization are of primary importance. Hydrodesulfurization is not limited by thermodynamic equilibrium at the usual process conditions. Furthermore, since the content of N and O components in mineral-oil fractions is relatively small, it seems to be reasonable to neglect the heteroatoms in calculating the energy of reaction. The calculation is restricted to equilibrium predictions of hydrogenation reactions of unsaturated hydrocarbons, which are equilibrium reactions.

Relevance of the DBE Concept in Hydroprocessing

The hydrogenation of an unsaturated hydrocarbon represented by F is expressed by

$$F + \nu_2 H_2 \rightleftharpoons P + \nu_4 H_2S + \nu_5 NH_3 + \nu_6 H_2O, \qquad (30)$$

where P is the product. Some fraction of the total hydrogen-consumption ν_2 is used for saturating the feedstocks. The amount of hydrogen that is used for feedstock saturation is equal to the reduction of DBE from the average feed to product molecule:

$$\nu_2 + \nu_4 + \frac{3}{2} \cdot \nu_5 \nu_6 \equiv \Delta \mathrm{DBE} = \mathrm{DBE}_P - \mathrm{DBE}_F. \qquad (31)$$

Since cracking of the C-C bonds is neglected in Eq. 30, the reaction follows the line of a constant number of carbon atoms. The atomic H/C ratio and the molecular-weight rise along this line, whereas the boiling temperature and DBE decrease, as is obvious from Figures 3 and 4.

Two examples are given in Tables 7 and 8. Table 7 contains data for the hydrodearomatization of a component with 25 carbon atoms and one aromatic ring, which is converted into a naphthenic ring, while in Table 8 a monoolefin is converted into a paraffine. The standard heat of reaction $(\Delta_R H^0)_H$, given in (kJ/mol hydrogen consumed) shown in these tables are values that are often used in the literature for approximating the heat of reaction for hydrotreating mineral oil fractions.

Equations 23 and 24 and Figure 8 imply that the absolute value of the hydrogen-based heat of reaction decreases with increasing DBE, which is in accordance with experimental observations (cf. Jaffe, Table 2, examples e, h, j, 1974). Analytical data and the characterization of a vacuum residue are shown in Table 9. The slight deviation between the values of the DBE of the feedstock obtained by the two different ways are within analytical errors. If the analytical H/C ratio in Table 9 represents an underestimate of about 3.2% (i.e., the C content would be 0.30 wt. % smaller and the H content would be 0.30 wt. % higher in reality), the value of the DBE obtained by means of Eq. 13 would be identical with the value obtained by Eq. 18.

Figure 10 shows typical results of characterization of the VGO and its hydrogenated product. Furthermore, the figure contains a number of pseudocomponents that have been generated on the basis of the feedstock boiling curve. If the H/C ratio distribution of the pseudocomponents is known, they can be characterized by means of the DBE concept. In Figure 1 the possible range of atomic H/C ratios is shown, which decreases slightly along the boiling range. The pseudocompo-

Table 6. Deviation from Experimental $\Delta_f H^0$ and $\Delta_f G^0$

	$\Delta_f H^0$	$\Delta_f G^0$
Number of data points	92	88
Average deviation in kJ/mol		
For optimum parameter θ_H and θ_G	0.45	0.45
For θ_i from Eqs. 25 and 29	6.72	3.24
(without alkyl-cyclohexanes)	2.82	
Maximum deviation in kJ/mol		
For optimum parameter θ_H and θ_G	1.95	2.12
For θ_i from Eqs. 25 and 29	8.38	4.33
(without alkyl-cyclohexanes)	4.07	

Table 7. Hydrogenation of an Aromatic Component

	Feed	Product
Number of carbon atoms, n	25	25
DBE	4	1
Number of olefinic double bonds, $\mathrm{DB_O}$	0	0
Molecular weight, M	344.6	350.7
Boiling point, T, °C	415	408
Stand heat of formation, $\Delta_f H^0$, kJ/mol	−325.8	−498.2
Standard heat of reaction: $\Delta_R H^0 = -172.4$ kJ/mol $(\Delta_R H^0)_H = -57.5$ kJ/mol H_2 consumed		

Table 8. Hydrogenation of an Olefinic Component

	Feed	Product
Number of C atoms, n	25	25
DBE	1	0
Number of olefinic double bonds, $\mathrm{DB_O}$	1	0
Molecular weight, M	350.7	352.7
Boiling point, T, °C	399	401
Stand heats of formation, $\Delta_f H^0$, kJ/mol	−434.6	−559.7
Standard heat of reaction: $\Delta_R H^0 = -125.1$ kJ/mol $(\Delta_R H^0)_H = -125.1$ kJ/mol H_2 consumed		

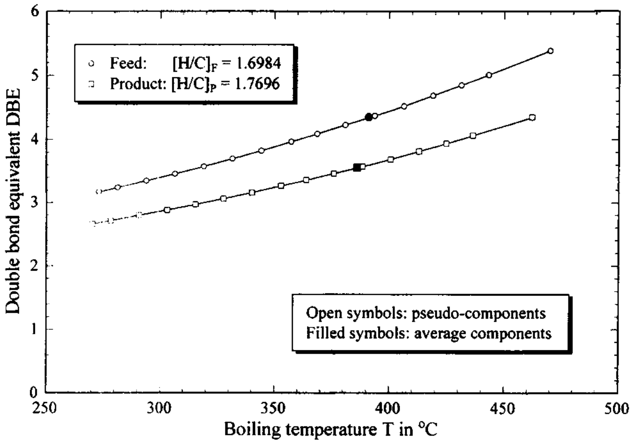

Figure 10. DBE of a mineral-oil fraction and the hydrotreated product.

nents shown in Figure 10 have been generated on the basis of a constant H/C ratio, which is a good approximation for narrow fractions. The H/C ratio of the product can be calculated by means of the mass balance

$$\left(\frac{\mathrm{C}}{\mathrm{H}}\right)_P=\frac{\left(\frac{\mathrm{C}}{\mathrm{H}}\right)_F}{1-\frac{\Delta\mathrm{DBE}}{w_\mathrm{H}^F}\cdot\frac{M_{\mathrm{H}_2}}{M_F}},\tag{32}$$

where w_H^F is the weight fraction of hydrogen in the feedstock:

$$w_\mathrm{H}^F=\frac{1-(w_\mathrm{S}^F+w_\mathrm{N}^F+w_\mathrm{O}^F)}{1+\left(\frac{\mathrm{C}}{\mathrm{H}}\right)_F\cdot\frac{M_\mathrm{C}}{M_\mathrm{H}}},\tag{33}$$

Table 9. Hydrogenation of Vacuum Residue

	Feed*	Product
Analytical data:		
Molecular weight, *M*	1,100	1,035
Elemental composition, wt. %		
C	82.24	88.46
H	10.17	11.51
S	6.40	0.0472
NMR analysis:		
Fraction of aromatic C atoms, C_A, %	22.7	15.0
Fraction of naphthenic C atoms, C_N, %	34.7	42.4
Fraction of paraffinic C atoms, C_P, %	42.6	42.6
Calculated data:		
Molar H/C ratio	1.474	1.551
Number of C atoms *n*	76.22	76.22
DBE (Eq. 13)	21.1	18.1
Structural data (Table 3):		
Number of aromatic rings, R_A	3.826	2.358
Number of naphthenic rings, R_N	6.612	8.080
Number of ring double bonds, DB_R	8.652	5.716
DBE (Eq. 18)	19.1	16.1
Boiling point *T*, °C	1,128	877
Standard heat of formation, $\Delta_f H^0$, kJ/mol	−760.7	−833.9
Standard heat of reaction:	$\Delta_R H^0 = -117.7$ kJ/mol $(\Delta_R H^0)_R = -22.9$ kJ/mol H_2 consumed	

*Analytical data from Völker (1992).

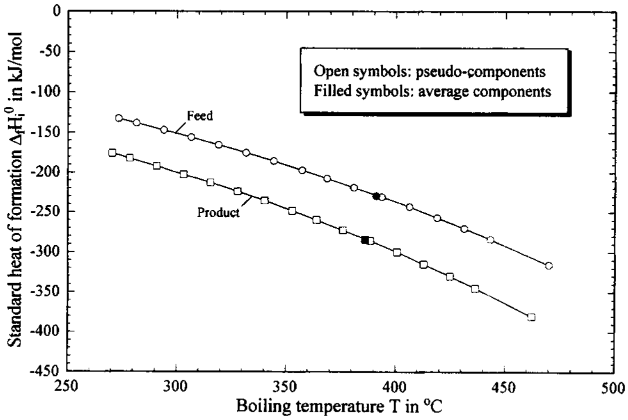

Figure 11. Standard heat of formation of the components shown in Figure 10.

and w_s^F, w_n^F, and w_O^F are the weight fractions of sulfur, nitrogen, and oxygen in the feedstock, respectively. According to Eq. 31 the value of ΔDBE is always negative if hydrogen is added to the feedstock.

The standard heat of formation and the standard Gibbs free energy of formation of the feed and product pseudocomponents shown in Figure 10 are graphically represented in Figures 11 and 12. All the properties of the mixture can be described by continuous functions.

Conclusions

A new procedure has been developed for characterizing hydrocarbon systems. The DBE can be calculated from any two of the properties, such as boiling point, atomic H/C ratio, molecular weight, or number of carbon atoms.

Aromatic hydrocarbons boil at higher temperatures than do paraffines with the same molecular weight. This dependence is numerically described by means of an excess temperature representing the deviation from the boiling point of the corresponding *n*-paraffine with the same number of C atoms as the component in question. The excess temperature is a function of the DBE, the number of olefinic double bonds DB_O, and the number of heteroatoms. Further properties, such as specific gravity and refractive index, depend on the molecular weight and DBE of the sample.

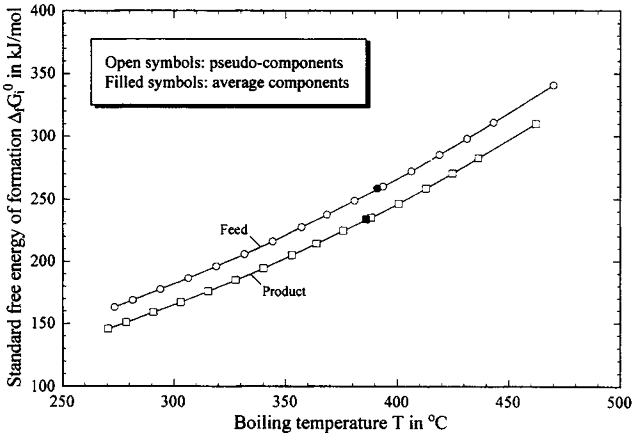

Figure 12. Standard free energy of formation of the components shown in Figure 10.

The DBE can be estimated from the properties mentioned earlier, and is also interconnected with the structural group distribution. Both methods deliver identical DBE values for pure hydrocarbons. The application to complex mineral-oil fractions where the structural group distribution was obtained by the *n-d-M* method and by NMR also shows good agreement. Deviations between a DBE calculated by using two different procedures are within analytical errors.

Heat-of-formation data are required to perform energy balances of reacting systems. Correlations for predicting the standard heat of formation as a function of molecular weight, the DBE, DB_O, and the number of heteroatoms are presented in this article.

Correlations are given for predicting the standard Gibbs free energy of formation from molecular weight, DBE, and DB_O. These data are essential for estimating chemical equilibria.

The application and relevance of the DBE concept are shown with regard to hydrogenation of pure hydrocarbons and high- and nonboiling mineral-oil fractions of unknown composition. The difference between the DBE values of feed and product is equivalent to the amount of hydrogen consumed for the hydrogenation of the unsaturated hydrocarbons. This enables us to estimate the DBE of the product by means of a mass balance; consequently, the properties of the product can be predicted. The heat of reaction is a function of the standard heat-of-formation data of the components involved. Since information about heat of formation of complex mineral-oil fractions was lacking in the past, average heat-of-reaction data with the dimension (kJ/mol H_2 consumed) have been used in the literature. These data are in agreement with the predictions for distillate fractions by means of the DBE concept.

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