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VISCOSITY OF SHC PROCESS
SHALE OIL BINARY BLENDS

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The temperature dependence of the kinematic viscosity for the solid heat carrier (SHC) process kukersite shale oils is described by a fundamental formula known for hydrocarbon oils. A viscosity matrix for the SHC process shale oils has been compiled. The evaluation of the kinematic viscosity of SHC process shale oil binary blends is discussed. It is shown that the viscosity of SHC process "gas turbine" oil fraction – commercial fuel oil blends can be evaluated by the standard blending calculation technique. Contrary to this, when "gas turbine" oil fraction or commercial fuel oil are blended with heavy SHC process shale oils (SES A and SEF B oils), the experimental values of blend kinematic viscosity are always higher than the calculated ones. For evaluation the difference between the experimental and calculated values of kinematic viscosity a simple equation can be used.

Estonian kukersite shale oil originated fuel oils are gaining more attention in both Estonia and abroad as effective diluents for residual petroleum oils.

The chemical group composition of petroleum and Estonian kukersite shale oils is fundamentally different: petroleum originated oils are principally made up of hydrocarbons, whereas shale oils are for the most part made up of oxygen compounds, especially of resorcinol series phenols, ketones and ethers. Due to the specific composition, associates (H-bond complexes) form between phenolic compounds as proton donors and ketones/ethers as proton acceptors.

Compared to conventional petroleum-originated fuel oils, the Estonian kukersite shale oil distillates have a very low vanadium content, a low pour point, good pumpability and a moderate sulfur content.

Nowadays there are two types of equipment employed for commercial processing of kukersite oil shale. Direct (internal) heated vertical shaft retorts (the *Kiviter* process) is a retort type to process large particle shale. As the heat carrier the process gas combustion products are used, being diluted

with cold semicoking gas. A special process, the SHC process (otherwise known as the *Galoter* process), has been developed for retorting shale fines. The SHC retort is a rotary kiln type retort. As the heat carrier the shale ash is used.

In the condensation (oil recovery) system of *Kiviter* retorts the shale oil produced is separated into two fractions – light-middle and heavy oils. The crude oil is diluted with its gasoline fraction and washed with water to remove water-soluble phenols, solid particles and corrosive salts (chlorides), and thereupon distilled into fractions. Ordinarily, the *Kiviter* shale oil distillation unit produces three distillate fractions: light "diesel oil" fraction (boiling range 180-230 °C), light gas oil fraction (boiling range 230-320 °C) and heavy gas oil fraction (boiling range 320-360 °C). Distillation residue is usually a coking feedstock.

The oil recovery system of SHC retorts is equipped with a special fractionating column, and redistillation of recovered oil is not used. Ordinarily, the following fractions are produced: gasoline fraction, "gas turbine" oil fraction, middle oil fraction and heavy oil fraction.

Shale oil originated commercial fuel oils are produced by blending redistilled (the *Kiviter* process oils) or recovered (the SHC process oils) fractions. Due to different conditions of oil recovery and fractionation, the chemical composition and standard distillation characteristics of oil fractions and their blends from the *Kiviter* and the SHC processes are also different.

In our previous paper [1], it was shown that for the kukersite shale oil distillates from the *Kiviter* process the temperature dependence of the kinematic viscosity is described with great accuracy by a fundamental formula accepted for hydrocarbon oil blends [2, 3]:

$$\log \log Z = A - B \log T \tag{1}$$

where Z is a function of the kinematic viscosity v (mm^2/s);

T is the temperature (K);

A and B are the viscosity characterization constants, whose values vary from one oil fraction to another.

If the kinematic viscosity exceeds 2.0 mm^2/s, one can approximate that

$$Z = v + 0.7 \ (\text{mm}^2/\text{s}) \tag{2}$$

When $v > 0.9$ mm^2/s, the function Z would accurately be represented as follows:

$$Z = v + 0.7 + C - D \tag{3}$$

where $C = \exp(-1.14883 - 2.65868 v)$;

$D = \exp(-0.0038138 - 12.5645 v)$.

Equations (1)–(3) hold true in spite of the fact that shale oils are not made up of hydrocarbons.

A viscosity matrix for shale oil distillates was also compiled.

In paper [4], it was shown that the kinematic viscosity of shale distillate oil blends from the *Kiviter* process can be evaluated by the standard blending calculation technique, accepted for hydrocarbon oil blends. There is only one exception: when the low-viscosity component is the light "diesel oil" fraction, the experimental values of blend kinematic viscosity are always higher than the calculated ones. In this event, the difference (Δ) between the logarithms of experimental (ν_{exp}) and calculated (ν_{calc}) values of blend kinematic viscosity depends on the volume fraction (φ) of component oils (H and L) as well as on ν_{exp}. This dependence may be expressed by a simple equation

$$\Delta = P\varphi_H\varphi_L + Q\varphi_H\varphi_L \log \nu_{exp} \qquad (4)$$

or

$$\frac{\Delta}{\varphi_H\varphi_L} = P + Q \log \nu_{exp}, \qquad (5)$$

where P and Q are constants that depend on the chemical nature of the component oils, but do not depend on component oil proportion.

This phenomenon was explained as a result of different chemical group composition of light "diesel oil" fraction and fractions with a boiling range above 230 °C.

This study deals with viscosity properties of shale oil fractions and their blends that are produced by retorting of the kukersite oil shale fines in SHC retorts.

Experimental

The temperature dependence of kinematic viscosity for shale oil fractions produced in SHC retorts and their blends was studied. Oil blends were attained by blending of fractions produced at Estonian Power Plant (the town of Narva).

The kinematic viscosity of the oils was determined in glass capillary viscometers as established by generally accepted standard specifications [5, 6]. For each oil fraction or blend the viscosity was measured, as minimum, at 6-8 various temperatures.

For calculation of blend's "theoretical" viscosity, the Wright standard method [2, 3] was used. Viscosities found using a computer technique [4], similar to that described by Huggins [7], are further interpreted as "calculated" values (ν_{calc}), contrary to the experimental ones (ν_{exp}) measured in laboratory. Compatibility of component oils and stability of blends were evaluated by standard spot test procedure [8].

Viscosity of the SHC process shale oils. It was found that for the kukersite shale oil produced in SHC retorts the temperature dependence of kinematic viscosity can be described by a fundamental Equation (1). If the kinematic

viscosity exceeds 2.0 mm^2/s, function Z can be calculated by Equation (2). When $\nu > 0.9$ mm^2/s, the function Z would accurately be represented by Equation (3).

Based on their own experiments, the authors have compiled a viscosity matrix for SHC shale oils. The latter includes the area from 5.0 mm^2/s at 20 °C (from 3.0 mm^2/s at 40 °C) to 180 mm^2/s at 50 °C, i.e. excluding the SHC process heavy oil fraction that has a high content of solid particles.

The matrix contains 25 base oils (from No. 5 to No. 29) whose viscosity characterization constants, A and B, are presented in Table 1.

Constants B characterize how drastically the viscosity of the oil depends on temperature. The greater the value for B the more the viscosity depends on temperature.

Constants B for shale oil fractions are, as a rule, greater than those of petroleum originated oils having the same viscosity at a standard temperature. In contrast to petroleum originated oils, the value of B for SHC process shale oils does not increase monotonously upon transition from one base oil to another. B attains its minimum value in the case of base oil No. 16, when at 50 °C the viscosity is 20 mm^2/s. For the *Kiviter* process shale oil distillates in [1] it was found that B attains its maximum value in the case of base oil No. 10.

The authors attribute this repugnance between the *Kiviter* and the SHC process oils to the different conditions of oil recovery and fractionation. In the *Kiviter* process distillate oils the concentration of resorcinol series

Table 1. **Viscosity Characterization Constants A and B for SHC Process Shale Oils**

Base oil No.	Nominal viscosity*	A	B	Base oil No.	Nominal viscosity*	A	B
00				17	25.00	9.77336	3.83524
01				18	30.00	10.19996	3.99601
02				19	35.00	10.54502	4.12606
03				20	40.00	10.83315	4.23464
04				21	50.00	11.29396	4.40831
05	3.00	10.59973	4.34547	22	60.00	11.65272	4.54352
06	4.00	10.37814	4.22747	23	70.00	11.85507	4.61784
07	6.00	10.10616	4.08259	24	80.00	12.01819	4.67755
08	8.00	9.63646	3.99220	25	100.00	12.28050	4.77357
09	10.00	9.81599	3.92804	26	120.0	12.48593	4.84876
10	12.00	9.72394	3.87901	27	140.0	12.65381	4.91022
11	10.00	9.65668	3.84318	28	160.0	12.79518	4.96196
12	12.00	9.56661	3.79521	29	180.0	12.91691	5.00652
13	14.00	9.49443	3.75676	30			
14	16.00	9.43460	3.72490	31			
15	18.00	9.38377	3.69783	32			
16	20.00	9.33976	3.67439				

* For base oils Nos. 05-10 the nominal viscosity is given at 40 °C and for base oils Nos. 11-29 at 50 °C.

phenols, a specific group component of kukersite shale oil, has a maximum value for fractions, the B for which is the greatest. The SHC process oils have a minimum concentration of oxygen compounds, if the viscosity at 50 °C is 16-20 mm^2/s. If the viscosity does not exceed 16 mm^2/s, oxygen compounds of SHC process oils are mainly made up of hydroxybenzene series phenols and ketones. Resorcinol series phenols consist in SHC process oils which have the viscosity higher than 20-24 mm^2/s.

Concentration of resorcin series phenols in the SHC process oils having high viscosity increases with increase of viscosity.

By using constants A and B from Table 1, it is possible to evaluate the kinematic viscosity of the SHC process shale oils in a wide temperature range (Table 2).

With the exception of the upper right hand corner of the table, which is sectioned off by a dotted dividing line, the values of viscosity in Table 2 have been calculated using Equation (2) for function Z. In the area above the dividing line, where $v < 2$, function Z has to be expressed by Equation (3). For the area in the lower left hand of the table, separated by a dotted line, experimental data do not exist. Therefore, the values of viscosity in this area

Table 2. **Viscosity of SHC Process Shale Oils**

Base oil No.	Viscosity, mm^2/s						
	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
05	5.01	3.81	**3.00**	2.43	2.02	1.71	1.47
06	7.03	5.20	**4.00**	3.18	2.59	2.16	1.84
07	11.37	8.07	**6.00**	4.63	3.68	3.00	2.50
08	16.00	11.04	**8.00**	6.04	4.72	3.79	3.11
09	20.88	14.07	**10.00**	7.43	5.72	4.53	3.69
10	25.96	17.16	**12.00**	8.79	6.68	5.24	4.23
11	30.70	20.00	13.81	**10.00**	7.53	5.87	4.69
12	38.90	24.81	16.83	**12.00**	8.92	6.87	5.44
13	47.53	29.78	19.89	**14.00**	10.29	7.84	6.16
14	56.54	34.88	22.99	**16.00**	11.65	8.80	6.86
15	65.90	40.11	26.13	**18.00**	12.99	9.74	7.54
16	75.59	45.45	29.30	**20.00**	14.32	10.66	8.21
17	111.2	62.60	38.26	**25.00**	17.26	12.48	9.37
18	156.0	82.41	47.85	**30.00**	20.03	14.09	10.34
19	208.7	104.2	57.87	**35.00**	22.70	15.59	11.23
20	269.5	128.0	68.29	**40.00**	25.28	17.01	12.04
21	415.9	181.1	90.17	**50.00**	30.25	19.65	13.52
22	596.6	241.3	113.3	**60.00**	35.00	22.07	14.84
23	794.1	304.1	136.8	**70.00**	39.72	24.51	16.18
24	1017	371.7	161.1	**80.00**	44.33	26.84	17.45
25	1545	520.9	211.8	**100.0**	53.23	31.20	19.77
26	2181	687.4	265.0	**120.0**	61.78	35.26	21.87
27	2925	870.1	320.5	**140.0**	70.05	39.08	23.81
28	3779	1068	378.1	**160.0**	78.08	42.71	25.61
29	4741	1281	437.4	**180.0**	85.91	46.17	27.30

Table 3. **The SHC Process Shale Oil Fractions Used for Blending**

Component shale oil	Component shale oil			
	"Gas turbine" oil fraction	Commercial fuel oil	SES A oil	SEF B oil
Density at 20 °C, kg/m^3	901.4	972.5	1019.8	1049.0
Flash point (closed cup), °C	55	26*	29	150*
Pour point, °C	-58	-34	-17	0
Water, %	0.27	0.43	0.52	0.68
Ash, %	0.02	0.35	0.81	0.14
Sulfur, %	0.90	0.81	0.86	0.58
Sediment, %	0	0	0.22	0.24
Constants of Eq. (1):				
A	10.66901	9.32334	11.67640	12.92720
B	4.38238	3.66564	4.55244	5.01029
Kinematic viscosity, mm^2/s:				
20 °C	4.547	79.64	611.5	4834
40 °C	2.760	30.60	115.1	442.9
50 °C	2.249	30.82	60.75	181.8
80 °C	1.381	8.475	14.93	27.44
Distillation, °C:				
IBP	150	85		
10 %	203	128		
50 %	228	310		
90 %	290	–		
FBP	330 (98 %)	365 (80 %)		

* Open cup.

of the table have been attained by extrapolation on Equations (1) and (2) without experimental verifications.

Viscosity of the SHC process shale oil binary blends. Oil blends were prepared by blending of SHC shale oil fractions produced commercially at Estonian Power Plant (Table 3).
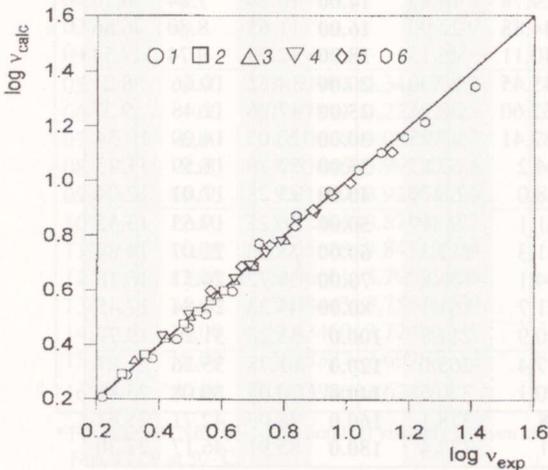
Fig. 1. Experimental (v_{exp}) and calculated (v_{calc}) values of kinematic viscosity (mm^2/s) for "gas turbine" oil fraction – commercial fuel oil binary blends.

Volume fraction high viscosity oil φ_H: *1* – 0.10, *2* – 0.20, *3* – 0.29, *4* – 0.40, *5* – 0.60, *6* – 0.80

From results obtained it follows that the kinematic viscosity of "gas turbine" oil fraction blends with commercial fuel oil can be evaluated by the standard blending calculation technique, accepted for hydrocarbon oil blends (Fig. 1). At all events, the differences between the experimental and calculated values of blend viscosity are not so essential that the standard calculation technique needs to be abandoned.

Contrary to this, for "gas turbine" oil fraction blends with SES A and SEF B oils, as well as for blends of commercial fuel oil with SES A and SEF B oils, the experimental values of kinematic viscosity are always higher than the calculated ones (Fig. 2).
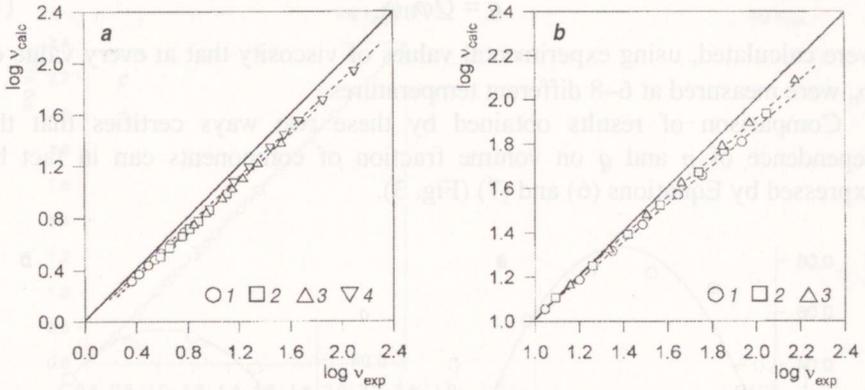
Fig. 2. Experimental (ν_{exp}) and calculated (ν_{calc}) values of kinematic viscosity (mm^2/s) for (*a*) "gas turbine" oil fraction – SEF B, and (*b*) commercial fuel oil – SES A oil binary blends.
Volume fraction high viscosity oil φ_H: *a*: *1* – 0.20, *2* – 0.40, *3* – 0.60, *4* – 0.80; *b*: *1* – 0.40, *2* – 0.60, *3* – 0.80

This phenomenon can be explained as a result of different group composition, on the one hand, of "gas turbine" oil fraction and commercial fuel oil, and, on the other hand, of SES A and SEF B oils. The formers are more similar to petroleum originated hydrocarbon oils than to a typical shale oil, whereas SES A and SEF B oils are mainly made up of oxygen compounds, especially of resorcinol series phenols, ketones and ethers.

Table 4. **Constants P and Q for SHC Process Shale Oil Binary Blends**

Low viscosity component	High viscosity component	P	Q	s_y*	$n**$
"Gas turbine" oil fraction	SES A oil	0.100 ± 0.024	0.214 ± 0.028	0.065	42
The same	SEF B oil	0.152 ± 0.023	0.341 ± 0.020	0.047	28
Commercial fuel oil	SES A oil	-0.672 ± 0.049	0.573 ± 0.030	0.045	21
The same	SEF B oil	-0.068 ± 0.035	0.206 ± 0.025	0.045	28

* $y = \Delta / \varphi_H \varphi_L$.
** Number of experimental values of blend viscosity.

Therefore the latters exhibit viscosity properties as a solution of associates ("polymers"), i.e. make contribution to the blend's viscosity according to their degree of association.

For these blends the difference Δ between the logarithms of v_{exp} and v_{calc} can be approximated by Equation (4). Constants P and Q were estimated for each blend oil (Table 4) by the least squares method as regression coefficients of Equation (5).

On the other hand, for each component oil proportion constants

$$p = P\varphi_H\varphi_L \qquad (6)$$

and

$$q = Q\varphi_H\varphi_L \qquad (7)$$

were calculated, using experimental values of viscosity that at every value of φ_H were measured at 6–8 different temperatures.

Comparison of results obtained by these two ways certifies that the dependence of p and q on volume fraction of components can in fact be expressed by Equations (6) and (7) (Fig. 3).
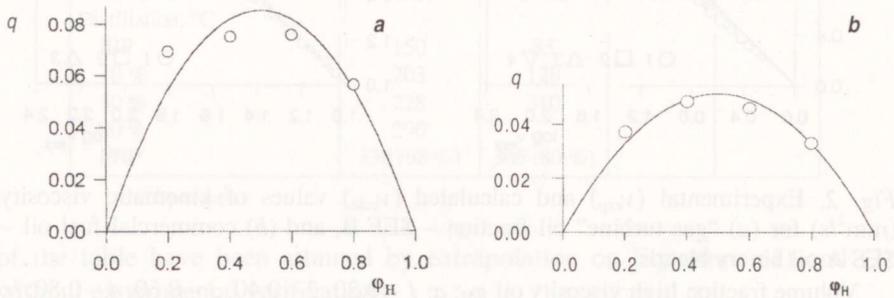
Fig. 3. Dependence of q on φ_H for (*a*) "gas turbine" oil fraction – SEF B and (*b*) commercial fuel oil – SEF B oil binary blends.

Curves – calculated, using constants P and Q from Table 4. Points – calculated, using at each φ_H value experimental values of v_{exp} at 6-8 various temperatures
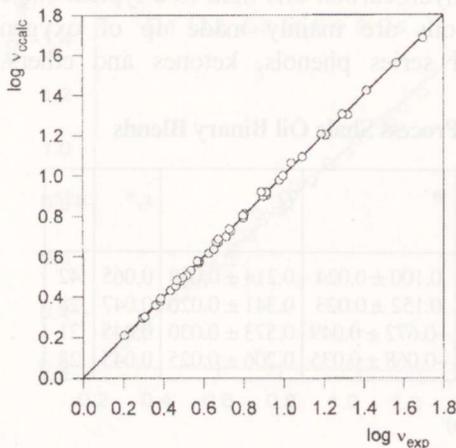
Fig. 4. Experimental (v_{exp}) and "corrected" calculated (v_{ccalc}) values of kinematic viscosity (mm^2/s) for "gas turbine" oil fraction – SES A oil blends.

Volume fraction high viscosity oil φ_H varies from 0.09 to 0.80
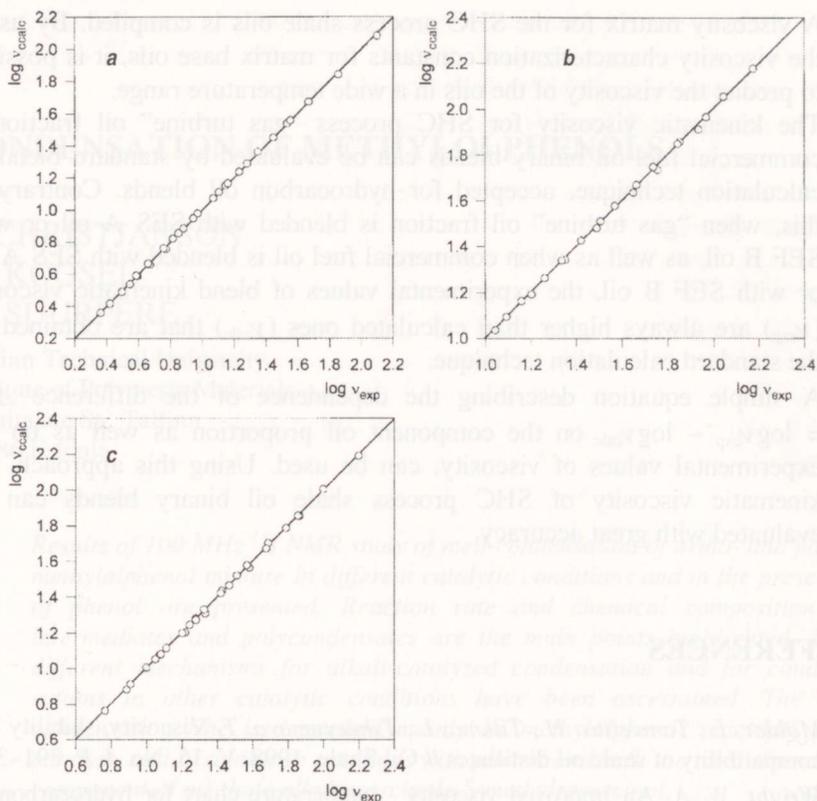
Fig. 5. Experimental (v_{exp}) and "corrected" calculated (v_{ccalc}) values of kinematic viscosity (mm^2/s) for (*a*) "gas turbine" oil fraction – SEF B, (*b*) commercial fuel oil – SES A, and (*c*) commercial fuel oil – SEF B oil blends.

Volume fraction high viscosity oil φ_H varies from 0.20 to 0.80 for *a* and *c*, and from 0.40 to 0.80 for *b*

Using values of *P* and *Q* from Table 4, the "corrected" calculated values of blend kinematic viscosity (v_{ccalc}) were obtained. Comparison of these values with the experimental ones confirms that for all blends a good accordance of v_{exp} and v_{ccalc} has been reached (Figs 4 and 5).

It must be also mentioned that all binary blends that are produced by blending of SHC process shale oils are stable at every ratio.

Conclusions

1. The kinematic viscosity of shale oils produced by retorting of the kukersite oil shale in SHC retorts is studied. It is shown that the temperature dependence of viscosity for all oil fractions can be described with great accuracy by a fundamental formula known for hydrocarbon oils.

2. A viscosity matrix for the SHC process shale oils is compiled. By using the viscosity characterization constants for matrix base oils, it is possible to predict the viscosity of the oils in a wide temperature range.

3. The kinematic viscosity for SHC process "gas turbine" oil fraction – commercial fuel oil binary blends can be evaluated by standard blending calculation technique, accepted for hydrocarbon oil blends. Contrary to this, when "gas turbine" oil fraction is blended with SES A oil or with SEF B oil, as well as when commercial fuel oil is blended with SES A oil or with SEF B oil, the experimental values of blend kinematic viscosity (v_{exp}) are always higher than calculated ones (v_{calc}) that are obtained by the standard calculation technique.

4. A simple equation describing the dependence of the difference $\Delta = \log v_{exp} - \log v_{calc}$ on the component oil proportion as well as on the experimental values of viscosity, can be used. Using this approach, the kinematic viscosity of SHC process shale oil binary blends can be evaluated with great accuracy.

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