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ANALYSIS OF THERMAL PROCESSES: THE EXPONENTIAL INTEGRAL

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Thermal processes can often be characterized by peak reaction temperatures, pre-exponentials, and activation energies, as well as by other parameters. Values of the exponential integral $Ei(-x)$, or of a related integral $I(x)$, where the numeric argument x is a function of activation energy and temperature, are essential to the analyses of many of these processes. It is shown that the use of only the first term of the concomitant asymptotic series to approximate these integrals can result in less reliability than the uncertainty in thermal reaction data. Hence, values of $I(x)$ which are accurate to 4 significant digits over the range of x from 15 to 50 are presented.

The exponential integral $Ei(-x)$ is frequently encountered in chemical kinetics, especially in cases involving the depletion of a species [1] due to a programmed temperature increase. In addition to the analysis of thermal desorption [2] data, which is of primary interest here, and where x is a function of the desorption energy and the temperature, the exponential integral and a related integral $I(x)$ are useful in the correlation of thermogravimetric [3], thermoluminescence [4, 5] and thermal oxidation [6] data with theoretical calculations. Values of $Ei(-x)$ and $I(x)$ are tabulated elsewhere [7–11], but there is insufficient range and detail in the argument x to permit analyses of thermal processes to be made to better than 14% to 16% accuracy for x from 15 to 50.

Thermogravimetric studies of gas–solid systems often result in measurements of Θ_s as a function of temperature T, where Θ_s is the fraction of an adsorbed state* remaining on the surface. It is advantageous to compare $d\Theta_s/dT$, which is the slope of the experimental Θ_s versus T curve, with the slopes calculated for a wide range of desorption parameters. The desorption parameters which characterize the process can then be chosen [2]. Some form of the Wigner–Polanyi [13] equation is usually assumed for thermal desorption processes, viz.,

$$-d\Theta_s/dt = v_\alpha \Theta_s^\alpha \exp(-E/RT), \tag{1}$$

where t is the time, α is the order of the desorption process, v_α is the frequency

* Θ_s should not be confused with Θ, which refers to a monolayer of adsorbed gas. The existence of several simultaneously adsorbed states on solid surfaces has been demonstrated [12].

factor, and E is the activation energy for desorption. Substituting $T = T_0 + \beta t$, where β is the heating rate, the temperature-equivalent form of Eq. (1) is

$$-\mathrm{d}\Theta/\mathrm{d}T = \nu_\alpha \Theta_s^\alpha/\beta \exp(-E/RT). \tag{2}$$

Integrating for $\alpha = 1$ and 2, Eq. (2) becomes

$$\left.\begin{array}{ll}\alpha = 1 & \ln \Theta_s/\Theta_{so} \\ \alpha = 2 & 1/\Theta_s - 1/\Theta_{so}\end{array}\right\} = \int\limits_{T_0}^{T} \exp(-E/RT)\mathrm{d}T = KI(x), \tag{3}$$

where the simplifications $K = \nu_\alpha E/\beta R$ and $x = E/RT$ have been used, and where $I(x)$ is in the form suggested by Smith and Aranoff [7]:

$$I(x) = \int\limits_0^{1/x} e^{-x}\,\mathrm{d}(1/x)\,. \tag{4}$$

A single integration by parts shows that this integral is related to the exponential integral.* Although Eq. (4) cannot be expressed in closed form, integration by parts n times results in an asymptotic series and a remainder integral; the series is then useful for approximating $I(x)$:

$$I(x) = e^{-x}/x^2\,[1 - 2!/x + 3!/x^2 - 4!/x^3 + \ldots + n!/x^{n-1}] + \\ + \int\limits_{-\infty}^{-x} \frac{(n+1)!}{r^{n+2}}\, e^r \mathrm{d}r\,. \tag{5}$$

Values of $\mathrm{d}\Theta_s/\mathrm{d}T$ can then be calculated from Eqs (2), (3), and (5), for a wide range of desorption parameters E and ν_α for physically realizable desorptions as determined by Θ_s, and compared with the experimental values of $\mathrm{d}\Theta_s/\mathrm{d}T$.

Comparisons of this kind for the silver–oxygen–carbon dioxide system [3] required values of $I(x)$ over a range of x from 15 to 50, in increments on x of 0.1. Interpolation between the values of $I(x)$ published for integral x resulted in as much as 16% error. Attempts were made to calculate $I(x)$ by a summation of incremental areas, and by Hastings' approximation [14]. Neither of these techniques were reliable for x greater than seven. Hence, an IBM Model 360 computer was used to sum up to sixteen terms of the series in Eq. (5) for $x = 10$ to 50, and the first through the sixteenth partial sums were printed.

Although asymptotic series are divergent, a limited number of terms of the series can be used to calculate a value of $I(x)$ to an accuracy which depends on x and the number of terms chosen [15]. Maximum bounds on the error thus incurred can be estimated by replacing e^r by e^{-x} in the remainder integral in Eq. (5). The maximum error, i.e., the difference between $I(x)$ and the sum of n terms of the series, is then given by

* $I(x) = e^{-x}/x + Ei(-x)$.

$$\epsilon_m = \frac{n!\, e^{-x}}{x^{n+1}} \, . \tag{6}$$

Differentiation of ϵ_m with respect to n for constant x, and the approximation of the resulting summation by an integral (for large n) yields the condition for maximum accuracy:

$$n = x - 1. \tag{7}$$

Hence, fourteen terms must be taken to obtain maximum accuracy for $x = 15$, whereas forty-nine terms are required at $x = 50$. Further analysis can be applied to show that ten terms are sufficient to obtain four significant digit accuracy over the range on x from 15 to 50. This is illustrated by Table 1; the divergent character of the series can also be seen from the 100 term column.

In Table 2, the results of summing ten terms of the series are given for x from 15 to 50 in increments of 0.1. It can be seen from Table 1 that the common use

Table 1

The maximum error ϵ_m incurred by taking the indicated number of terms for specified values of x. $E_{\bar{p}}$ indicates multiplication by 10^{-p}

	1 term		10 terms	
x	$I(x)$	ϵ_m	$I(x)$	ϵ_m
10	0.4540 E $\bar{6}$	0.4540 E $\bar{8}$	0.3822 E 6	0.0016 E $\bar{6}$
15	0.1306 E $\bar{8}$	0.1306 E $\bar{8}$	0.1207 E $\bar{8}$	0.0009 E $\overline{10}$
20	0.5153 E $\overline{11}$	0.5153 E $\overline{11}$	0.4702 E $\overline{11}$	0.0004 E $\overline{13}$
30	0.1040 E $\overline{15}$	0.1040 E $\overline{15}$	0.9766 E $\overline{16}$	0.0192 E $\overline{21}$
40	0.2655 E $\overline{20}$	0.2655 E $\overline{20}$	0.2532 E $\overline{20}$	0.0037 E $\overline{26}$
50	0.7715 E $\overline{25}$	0.7715 E $\overline{25}$	0.7424 E $\overline{25}$	0.0143 E $\overline{32}$

	16 terms		100 terms	
x	$I(x)$	ϵ_m	$I(x)$	ϵ_m
10	0.3771 E $\bar{6}$	0.0095 E $\bar{6}$	unknown	4.23×10^{52}
15	0.1207 E $\bar{8}$	0.0005 E $\overline{10}$	unknown	3.33×10^{32}
20	0.4703 E $\overline{11}$	0.0003 E $\overline{14}$	unknown	7.55×10^{17}
30	0.9766 E $\overline{16}$	0.0151 E $\overline{23}$	unknown	5.64×10^{-5}
40	0.2532 E $\overline{20}$	0.0519 E $\overline{30}$	unknown	6.18×10^{-22}
50	0.7424 E $\overline{25}$	0.0528 E $\overline{38}$	unknown	4.55×10^{-36}

Table 2

$I(x)$ as a function of the exponential argument x, using ten terms in the series. The asterisk, where it appears, means that the multiplier is to be applied to those terms to its right

Multiplier	x	0	.1	.2	.3	.4	.5	.6	.7	.8	.9
10^{-9}	15	.1207	.1079	*.9639	.8614	.7698	.6881	.6151	.5498	.4916	.4395
	16	.3930	.3514	.3142	.2810	.2513	.2248	.2011	.1799	.1609	.1440
10^{-10}	17	.1288	.1153	.1032	*.9231	.8261	.7394	.6618	.5924	.5303	.4747
	18	.4250	.3805	.3407	.3051	.2732	.2446	.2191	.1962	.1758	.1574
10^{-11}	19	.1410	.1263	.1132	.1014	*.9083	.8138	.7292	.6534	.5855	.5247
	20	.4702	.4214	.3777	.3386	.3035	.2720	.2439	.2186	.1960	.1757
10^{-12}	21	.1575	.1413	.1267	.1136	.1018	*.9133	.8191	.7346	.6588	.5909
	22	.5300	.4754	.4265	.3826	.3432	.3079	.2762	.2478	.2223	.1995
10^{-13}	23	.1790	.1606	.1441	.1293	.1161	.1042	*.9349	.8390	.7530	.6759
	24	.6067	.5446	.4888	.4388	.3939	.3536	.3175	.2850	.2559	.2297
10^{-14}	25	.2063	.1852	.1663	.1493	.1341	.1204	.1081	*.9712	.8722	.7833
	26	.7035	.6318	.5675	.5097	.4579	.4113	.3694	.3319	.2981	.2678
10^{-15}	27	.2406	.2161	.1942	.1745	.1567	.1408	.1265	.1137	.1022	*.9180
	28	.8249	.7413	.6661	.5986	.5379	.4834	.4345	.3905	.3510	.3154
	29	.2835	.2548	.2290	.2059	.1851	.1663	.1495	.1344	.1208	.1086
10^{-16}	30	*.9766	.8780	.7893	.7096	.6380	.5736	.5157	.4637	.4169	.3749
	31	.3371	.3031	.2726	.2451	.2204	.1982	.1782	.1603	.1442	.1296

10^{-17}	32	.1166	.1049	*.9431	.8482	.7629	.6862	.6172	.5551	.4993	.4491
	33	.4040	.3634	.3269	.2941	.2645	.2380	.2141	.1926	.1733	.1559
10^{-18}	34	.1402	.1262	.1135	.1021	*.9188	.8267	.7438	.6693	.6022	.5419
	35	.4876	.4387	.3948	.3552	.3197	.2877	.2589	.2330	.2096	.1887
10^{-19}	36	.1698	.1528	.1375	.1238	.1114	.1002	*.9022	.8120	.7309	.6578
	37	.5921	.5329	.4797	.4318	.3887	.3498	.3149	.2835	.2552	.2297
10^{-20}	38	.2068	.1861	.1676	.1508	.1358	.1223	.1101	*.9909	.8921	.8031
	39	.7230	.6510	.5861	.5277	.4751	.4278	.3852	.3468	.3123	.2812
10^{-21}	40	.2532	.2280	.2053	.1848	.1664	.1499	.1350	.1215	.1094	*.9855
	41	.8874	.7992	.7197	.6481	.5837	.5256	.4734	.4263	.3840	.3458
	42	.3114	.2805	.2526	.2275	.2049	.1846	.1662	.1497	.1349	.1215
10^{-22}	43	.1094	*.9855	.8877	.7996	.7203	.6488	.5844	.5264	.4742	.4272
	44	.3848	.3466	.3123	.2183	.2534	.2283	.2057	.1853	.1669	.1504
10^{-23}	45	.1355	.1220	.1099	*.9906	.8924	.8040	.7244	.6527	.5880	.5298
	46	.4773	.4301	.3875	.3491	.3146	.2835	.2554	.2301	.2074	.1868
10^{-24}	47	.1684	.1517	.1367	.1232	.1110	.1000	*.9012	.8121	.7318	.6595
	48	.5943	.5355	.4826	.4349	.3919	.3532	.3183	.2869	.2585	.2330
10^{-25}	49	.2100	.1892	.1705	.1537	.1385	.1248	.1125	.1014	*.9139	.8237
	50	.7424									

of only the first term in the series can result in 8% error, and a comparison between any quantity in Table 2 and the number obtained by linear interpolation between the two corresponding values of $I(x)$ for integral x shows that a 14% to 16% difference results from such interpolation. Since thermal desorption data are often reliable to 5% or better, the information in Table 2 is essential to any comparison of experimental data with the Wigner–Polanyi equation.

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RÉSUMÉ — On peut souvent caractériser les processus thermiques par la température des pics réactionnels, les facteurs pré-exponentiels, les énergies d'activation et autres paramètres. La valeur de l'intégrale exponentielle $Ei(-x)$, ou d'une intégrale qui s'y rattache $I(x)$, où x est une fonction de l'énergie d'activation et de la température, est essentielle pour l'étude d'un grand nombre de ces processus. On montre que l'emploi du premier terme seulement de la série asymptotique convergente comme première approximation de ces intégrales peut conduire à un manque d'exactitude supérieur à celui provenant des données thermiques. On présente ainsi des valeurs de $I(x)$ avec 4 chiffres significatifs dans le domaine de x allant de 15 à 50.

ZUSAMMENFASSUNG — Thermische Vorgänge können oft durch Spitzenreaktionstemperaturen, präexponentiellen Faktoren, Aktivierungsenergien oder andere Parameter gekennzeichnet werden. Werte des exponentiellen Integrals $Ei(-x)$ oder eines entsprechenden Integrals $I(x)$, wobei x die Funktion von Aktivierungsenergie und Temperatur ist, sind wichtig zur Analyse vieler dieser Prozesse. Es wurde gezeigt, daß die Benutzung nur des ersten Gliedes der sich nähernden asymptotischen Serie zur Approximation dieser Integrale in geringerer Verläßlichkeit resultiert als die Unsicherheit der thermischen Daten. Werte von $I(x)$, die genau auf 4 signifikante Zahlenwerte über den Wert von x von 15 bis 50 zutrafen, wurden vorgelegt.

Резюме — Термические процессы часто характеризуют экстремальной температурой реакции, предэкспоненциальным множителем, энергией активации и другими параметрами. Величина экспоненциального интеграла $Ei(-x)$, или отнесенного интеграла $I(x)$, где цифровое значение x является функцией энергии активации и температуры, важно для анализа многочисленных процессов сходного типа. В статье даны величины $I(x)$ с точностью до 4-го знака выше области x от 15 до 50.