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The relationship between oxidation induction temperatures and times for petroleum products

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Abstract

Differential scanning calorimetry (DSC) is an established technique for comparing the oxidation stabilities of substances that contain oxidation inhibitors, e.g. lubricants and polyolefins, for quality control and research purposes. Two types of data can be obtained from DSC: induction times or induction temperatures. A relationship between the two is derived from the Arrhenius equation and, assuming an activation energy of 140 kJ mol^{-1}, this is used to predict induction times from induction temperatures for a variety of materials. The predictions agree with experiment to within ±15%.

One application of the relationship will be to use an induction temperature to predict the optimal temperature for an isothermal experiment. At a more ambitious level, oxidation induction points could be transformed from the temperature to the time domain.

INTRODUCTION

Differential scanning calorimetry (DSC) has become established in industry as an accelerated-oxidation technique for comparing the stabilities of hydrocarbon products which contain oxidation inhibitors. These products include lubricating oils, edible oils, greases and polymers, where the inhibitor prevents oxidation during processing, storage or service.

There are several DSC methods in use, some using high-pressure oxygen or air to minimise the vaporisation of a volatile sample, some using added catalysts or catalytically active pans to simulate service conditions. However, in the present context, the important distinction is between experiments run at a fixed temperature (isothermal mode) to give an oxidation induction time and those run at a fixed rate of temperature change (scanning mode) to give an oxidation induction temperature.

Typical DSC curves for a scanning and an isothermal experiment are shown in Figs. 1 and 2.

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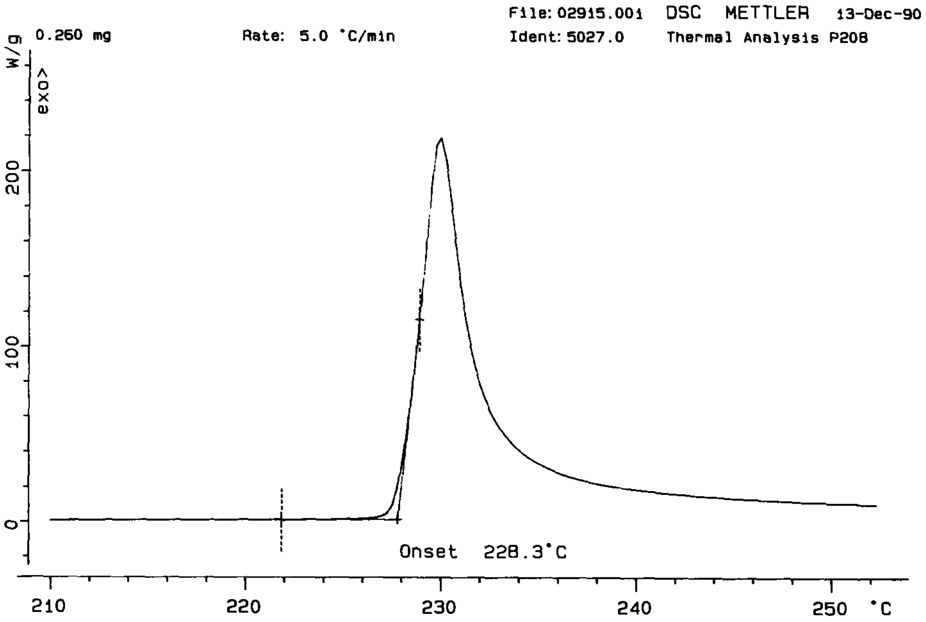

Fig. 1. Scanning DSC curve for a lubricating oil which contains an inhibitor. Conditions: 0.26 mg oil in Al pan; 35 bar O_2; start at 100°C; 5 K min^{-1}.

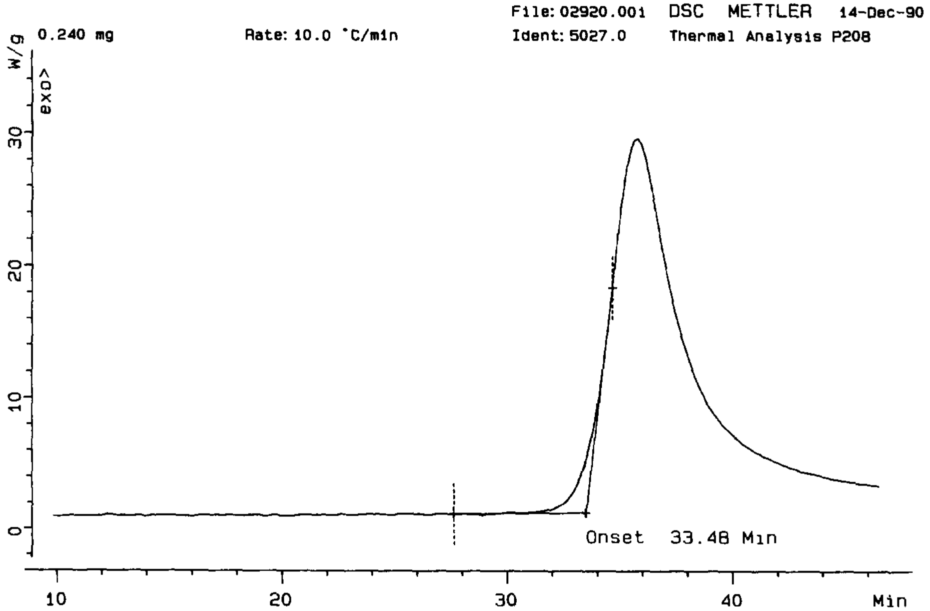

Fig. 2. Isothermal DSC curve for lubricating oil which contains an inhibitor. Conditions: 0.24 mg oil in Al pan; 35 bar O_2; start at 100°C; 10 K min^{-1}; hold at 195°C.

The isothermal mode can be experimentally problematic because it requires the selection of a suitable temperature: if too low or too high, induction times will be impractically long or short. This is not a problem with the scanning mode, which almost always gives a result within the range 100–300°C. However, induction times can be related to service lifetimes whereas induction temperatures can only be used to order the members of a set of oils, and for this reason the isothermal data are generally preferred.

It should be noted that substances which do not contain oxidation inhibitors, e.g. base oils, will give no significant induction time and can only be compared by the scanning mode.

Clearly the ideal arrangement would be to measure an induction temperature and calculate from this an induction time. However, at a less ambitious level, it would be very useful to use an induction temperature to calculate a suitable temperature for an isothermal run and thereby avoid time-wasting trial and error. These considerations lead to the question: what is the relationship between induction times and induction temperatures? The answer and its practical significance are discussed below.

DERIVATION OF THE RELATIONSHIP

The oxidation inhibitors in petroleum products (and some other hydrocarbons) are of two types: primary, such as hindered phenols or aromatic amines, which remove peroxyl radicals ($ROO^{\cdot}$); and secondary, such as zinc dialkyl dithiophosphate, which decompose the autocatalytic hydroperoxides (ROOH). According to Barnes and Bell [1], the oxidation rate of a thin film of oil in a DSC experiment is limited by the rate of spontaneous initiation until either type of inhibitor reaches a critically low value, and if both types of inhibitor operate efficiently, the limiting reaction can be written as

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}$$

Taking this as the starting point, the corresponding rate equation is

$$-\mathrm{d}[RH]/\mathrm{d}t = [RH][O_2]A \exp(-E_a/RT) \tag{1}$$

where [RH] is the concentration of the hydrocarbon, $[O_2]$ is the concentration of dissolved O_2, A is the pre-exponential factor, E_a is the activation energy, t is time, T is thermodynamic temperature, and R is the gas constant. In the following, it will be assumed that $[O_2]$ does not vary significantly with temperature at a fixed pressure of O_2 compared to the temperature dependence of the reaction rate. This then allows $[O_2]$ to be treated as a constant.

Separating the variables gives eqn. (2), which is applicable to an isothermal experiment at temperature T_{iso}.

$$-(1/(A[O_2]))\int(1/[RH])\,\mathrm{d}[RH] = \exp(-E_a/RT_{iso})\int \mathrm{d}t \tag{2}$$

Equation (1) can be rearranged for the case of an experiment at a scanning rate of $\beta = \mathrm{d}T/\mathrm{d}t$ to give

$$-\mathrm{d}[\mathrm{RH}]/\mathrm{d}T = (1/\beta)[\mathrm{RH}][\mathrm{O_2}]A\ \exp(-E_a/RT) \tag{3}$$

and the variables can be separated to give

$$-(1/(A[\mathrm{O_2}]))\int(1/[\mathrm{RH}])\ \mathrm{d}[\mathrm{RH}] = (1/\beta)\int\exp(-E_a/RT)\ \mathrm{d}T \tag{4}$$

The next step is to assume that during the induction period, [RH] falls from an initial value of $[\mathrm{RH}]_0$ to a critically low value $[\mathrm{RH}]_{\mathrm{ind}}$, and that $[\mathrm{RH}]_{\mathrm{ind}}$ depends only on the amount of anti-oxidant present. That is, at the point where the anti-oxidant is depleted, $[\mathrm{RH}]_{\mathrm{ind}}$ has the same value in both the isothermal and scanning experiments. This point is at induction time t_{ind} in the isothermal run and at induction temperature T_{ind} in the scanning run. Then the integration limits in eqn. (2) can be set at $[\mathrm{RH}]_0$ and $[\mathrm{RH}]_{\mathrm{ind}}$, and $t = 0$ and $t = t_{\mathrm{ind}}$; and in eqn. (4) at $[\mathrm{RH}]_0$ and $[\mathrm{RH}]_{\mathrm{ind}}$, and $T = 0$ and $T = T_{\mathrm{ind}}$. When this is done, the left-hand sides of eqns. (2) and (4) are equal, so the right-hand sides can be equated to give

$$\exp(-E_a/RT_{\mathrm{iso}})\int_0^{t_{\mathrm{ind}}}\mathrm{d}t = (1/\beta)\int_0^{T_{\mathrm{ind}}}\exp(-E_a/RT)\ \mathrm{d}T \tag{5}$$

Integrating the left side of eqn. (5) and rearranging gives the desired relationship

$$t_{\mathrm{ind}} = \{1/[\exp(-E_a/RT_{\mathrm{iso}})\beta]\}\int_0^{T_{\mathrm{ind}}}\exp(-E_a/RT)\ \mathrm{d}T \tag{6}$$

Equation (6) relates the oxidation induction time for an isothermal run at T_{iso} to the oxidation induction temperature for a scanning run at a heating rate of β. It is only applicable if two conditions are satisfied: (a) The sample contains an oxidation inhibitor. (b) All variables, e.g. sample size and gas pressure, are the same for the isothermal and scanning experiments.

ACTIVATION ENERGIES

If eqn. (6) is to be used to relate oxidation induction temperatures to times, it is obviously necessary to know the activation energy E_a for the initiation reaction. For a particular oil under specified conditions, the activation energy is usually derived by measuring induction times at several fixed temperatures and fitting the data by linear regression to

$$\ln(t_{\mathrm{ind}}) = a + E_a/RT \tag{7}$$

This equation, which is essentially a rearrangement of the integrated form of eqn. (2), provides a good fit in most cases [1–3] as exemplified by the data in Table 1.

TABLE 1

Arrhenius data [a]

Sample	Number of measurements	E_a (kJ mol^{-1})	Corr. coef.
Lube oil 4	5	135	0.973
Lube oil 14	25	168	0.994
Lube oil 15	25	120	0.999
Lube oil 16	25	153	0.995

[a] The experimental details are given in the section headed Samples and conditions.

Activation energies obtained in this way by DSC or similar techniques typically fall in the range 140 ± 30 kJ mol^{-1} (the average value in Table 1 is 144 kJ mol^{-1}). This corresponds to known values of $\approx$ 140 kJ mol^{-1} for the reaction in eqn. (1) [1]. Note that in Table 1 the sample and conditions for lube oil 15 are the same as for 14 but with catalyst added; this decreases the activation energy as expected.

IMPLEMENTING THE RELATIONSHIP

Having selected an activation energy, the next problem is the evaluation of the integral in eqn. (6): there is no exact solution for this, and while there are some approximations in the literature, it is simpler to integrate numerically on a computer. To simplify the integration, the lower temperature limit can be set to 100 K below T_{iso}, rather than zero, because there will be no significant reaction at this temperature. The program in Appendix 1 prompts the user for an induction temperature and corresponding heating rate; an isothermal temperature can then be entered and the induction time calculated.

TESTING THE RELATIONSHIP

Equation (6) was tested by comparing experimental induction times with those calculated from induction temperatures for: (a) the four oils in Table 1, using the experimental activation energies; and (b) a wide range of petroleum products, assuming a typical activation energy of 140 kJ mol^{-1}.

Samples and conditions

The samples were 16 lubricating oils, two gasolines and one grease; all were fully formulated products which contained oxidation inhibitors as well as other additives.

Heating rates ranging from 1 to 10 K min^{-1} were used but in most cases the choice was 5 K min^{-1}. The sample size, presence of a liquid catalyst or catalytically active crucible, and type and pressure of the atmosphere were selected as those most widely used for the particular material in this or other laboratories.

All experiments were run using a Mettler high-pressure DSC20 with aluminium pans, unless otherwise indicated. The Mettler software corrects for thermal lags at different heating rates; this was confirmed by melting indium at 1, 2 and 10 K min^{-1}. For high-pressure runs, a static atmosphere was used; for ambient-pressure runs, the atmosphere flowed through the furnace at 100 cm^3 min^{-1} STP.

The samples and conditions were as follows. (a) Grease: 2 mg; 35 bar O_2. (b) Gasolines 1, 2: 1 mg in pan with ambient O_2, sealed to prevent loss of vapour. (c) Lube oils 1, 2: 0.2 mg; 35 bar O_2. (d) Lube oil 3: same oil and conditions as lube oil 1 but with liquid Cu–Fe catalyst. (e) Lube oils 4–7: 3 mg in carbon steel pan; 1 bar air. (f) Lube oils 8–13: 3 mg in pure iron pan; 1 bar air. (g) Lube oil 14: 1.5 mg; 35 bar O_2. (h) Lube oil 15: 1.5 mg of same oil as lube oil 14 but with a liquid Cu–Fe catalyst; 35 bar O_2. (i) Lube oil 16: 1.5 mg of same oil as lube oil 14; 35 bar air.

In all cases except the gasolines, the induction time or temperature was calculated as the intersection of the baseline with a tangent to the curve at its steepest point. The steepest point was determined from the first derivative curve. The values obtained in this way are independent of the operator. For the gasolines, the onsets were too broad for this procedure, but peaks were unambiguous and these were used. Typical repeatability for onset temperatures is ±1 K, and ±1 min for times.

Table 2 gives the experimental and calculated induction times and their differences for the oils whose activation energies are known and given in Table 1. Statistically, there is agreement at the 80% level between these small sets, but obviously more data would be needed for a conclusive confirmation.

Table 3 compares experimental results with predictions based on an activation energy of 140 kJ mol^{-1}. A statistical analysis of the differences, i.e. experimental–calculated, gives a mean of +1.2 min and a standard

TABLE 2

Comparisons of experimental with computer-calculated induction times using experimentally determined values for E_a [a]

Sample	E_a (kJ mol^{-1})	T_{iso} (°C)	Induction time (min)		
			Expt.	Calc.	Diff.
Lube oil 4	135	225	7	7	0
Lube oil 14	168	185	27	38	+11
Lube oil 15	120	175	35	37	+2
Lube oil 16	153	195	27	30	−3

[a] The experimental details are given in the section headed Samples and conditions.

TABLE 3

Comparisons of experimental with computer-calculated induction times assuming $E_a = 140$ kJ mol^{-1} [a]

Sample	T_{ind} (°C)	β (K min^{-1})	T_{iso} (°C)	Induction time (min)		
				Expt.	Calc.	Diff.
Grease	204.4	5	174	38	28	−10
Gasoline 1 [b]	123 [p]	1	125	11 [p]	7 [p]	−4
Gasoline 2 [b]	138 [p]	1	125	40 [p]	37 [p]	−3
Lube oil 1	222.7	10	185	26	22	−4
	216.4	5	185	26	28	+2
	204.3	2	185	26	29	+3
Lube oil 2	228.3	5	195	33	31	−2
	217.8	2	195	33	36	+3
Lube oil 3	201.3	5	170	30	31	+1
Lube oil 4 [c]	237.0	5	225	7	7	0
Lube oil 5 [c]	260.0	5	225	26	30	+4
Lube oil 6 [c]	267.0	5	225	48	46	−2
Lube oil 7 [c]	263.0	5	225	36	36	0
Lube oil 8 [d]	242.0	5	205	36	38	+2
Lube oil 9 [d]	239.1	5	205	25	31	+6
Lube oil 10 [d]	251.4	5	205	59	69	+10
Lube oil 11 [e]	263.5	5	230	24	26	+2
Lube oil 12 [e]	260.3	5	230	21	21	0
Lube oil 13 [e]	250.4	5	230	11	14	+3
Lube oil 14 [f]	216.5	5	185	27	29	+2
Lube oil 15 [f]	212.3	5	175	35	48	+13
Lube oil 16 [f]	226.1	5	195	27	26	+1

[a] The experimental details are given in the section headed Samples and conditions.

[b,c,d,e] Samples run as a set for intercomparison.

[f] One oil, three sets of conditions.

[p] Peak temperatures used.

deviation of 4.8 min (≈ 15% of the experimental value). The optimum E_a i.e. giving a zero average difference, was found to be 135 kJ mol^{-1}.

Apart from the use of an average value for E_a, there is another major source of error in this work: the identification of the end of the induction period. Ideally this should be taken as the point where there is a given amount of reaction, e.g. 1%, or, more practically, the time or temperature corresponding to a chosen heat of reaction. However, such data analysis is impractical for most laboratories.

CONCLUSIONS

The procedure described here represents a scientifically based, practically useful approach to the problem of using an induction temperature to select a suitable temperature for an isothermal experiment.

The relationship also opens up the possibility of transforming oxidation induction points from the temperature to the time domain for samples or sets of samples which do not give significant signals in isothermal DSC experiments.

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APPENDIX

A program in C to calculate an induction time at a chosen isothermal temperature from a given induction temperature and heating rate.

```
#include <stdio.h>
#include <math.h>
#define Ea 140000 /*  kJ/mol   */
#define R 8.314
#define dT 0.25 /* temperature step for integration */

main()
{

int restart=1;
float T_iso,T_ind,time_ind,T=0,heating_rate,sum;

printf("\n\n\n%s\n%s\n%s\n\n\n",
 "Predicts an induction time at a selected isothermal temperature",
 "using a measured induction temperature ",
 "at a known heating rate.");

while(restart)
   {
   printf("\n\n\nGive induction temperature (C): ");
   scanf("%f",&T_ind);
   T_ind+=273; /* convert to kelvin */
   printf("Give heating rate (C min-1): ");
   scanf("%f",&heating_rate);

   while(1)
      {
      printf("Give isothermal temperature (C) (zero to quit): ");
      scanf("%f",&T_iso);
         if(T_iso<=0.0)
           break;
      T_iso+=273;
      sum=0;

           for(T=200;T<=T_ind;T+=dT)
              sum+=exp(-Ea/T/R);

      time_ind=sum/(exp(-Ea/R/T_iso))/heating_rate*dT;

      printf("\n\nInduction time: %.1f min \n",time_ind);
      }

   printf("Re-start the programme? .... 1=yes  0=no  ");
   scanf("%d",&restart);
   }
}
```