Pressure Differential Scanning Calorimetry (PDSC)

Ford METS, 2/26/2014

Arsen Terjimanian

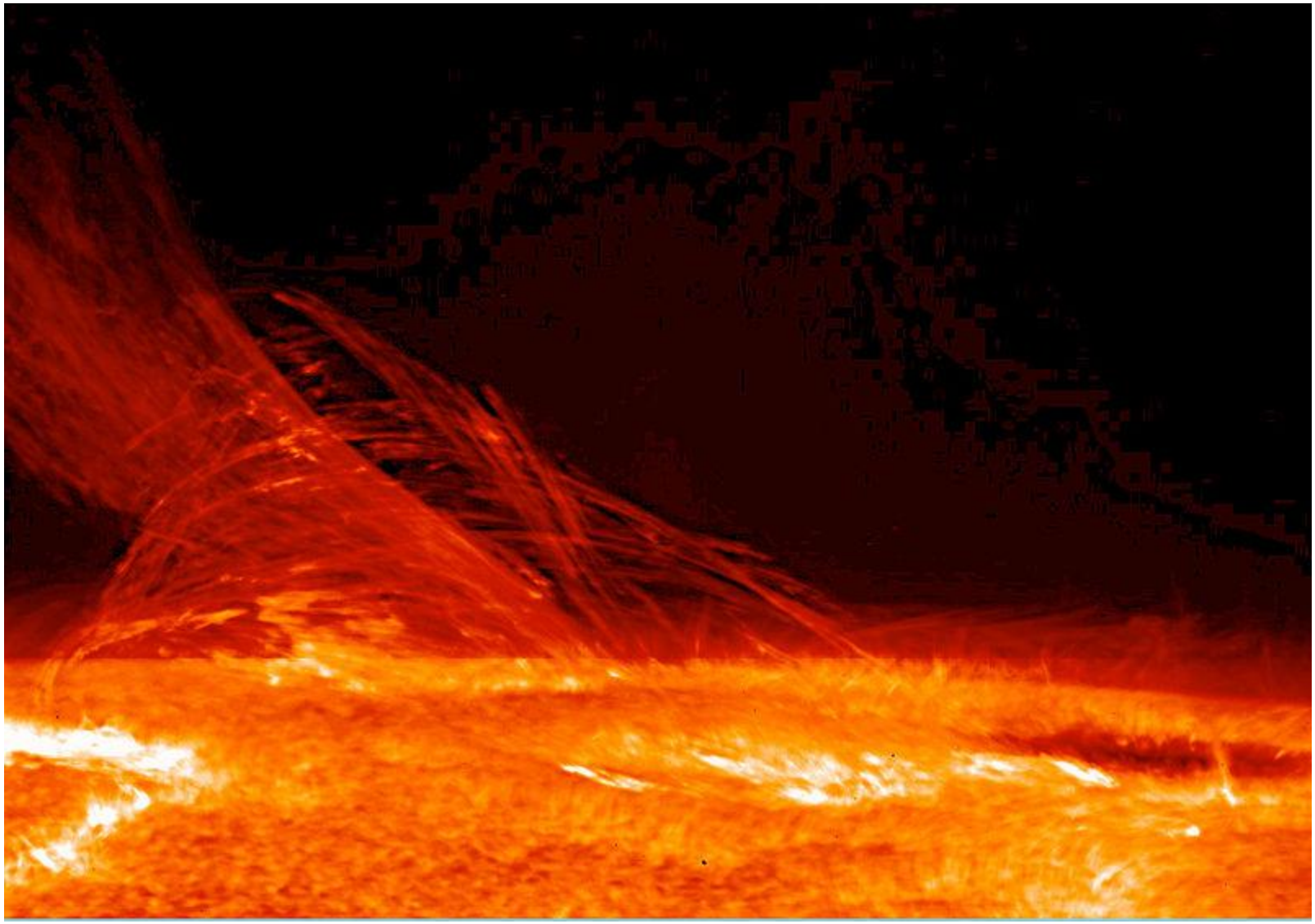
Outline

- Historical background: Why PDSC?
- Some common terms about heat (what's heat and what's temperature?)
- DSC
- PDSC
- Experimental outcomes
- Test procedures
- Summary
- Questions

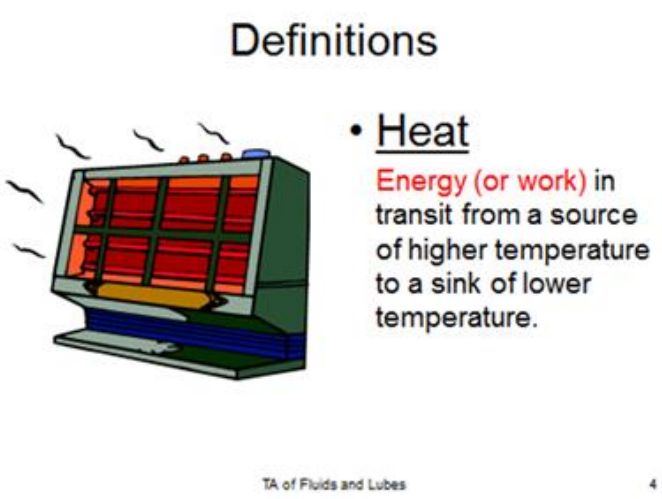
Historical Background

- Issue: Predictive Life Testing of P/S Hoses
- ASTM Technical Reports SR-93-199, SR-94-164, SR 94-165 by R. Pett and M. Nichols of Ford SRL: Isothermal DSC to determine Activation Energy from Polymer Oxidation
- Ford CL (Doyle, Edmonson, Mehandru, Nguyen, Hoffman): Numerous DSC runs over 100s of hours but no exotherm; no Activation Energy values
- Outcome: DSC not a good technique (2/21/1996)
- New Plan: Investigate Pressure DSC

HEAT



HEAT



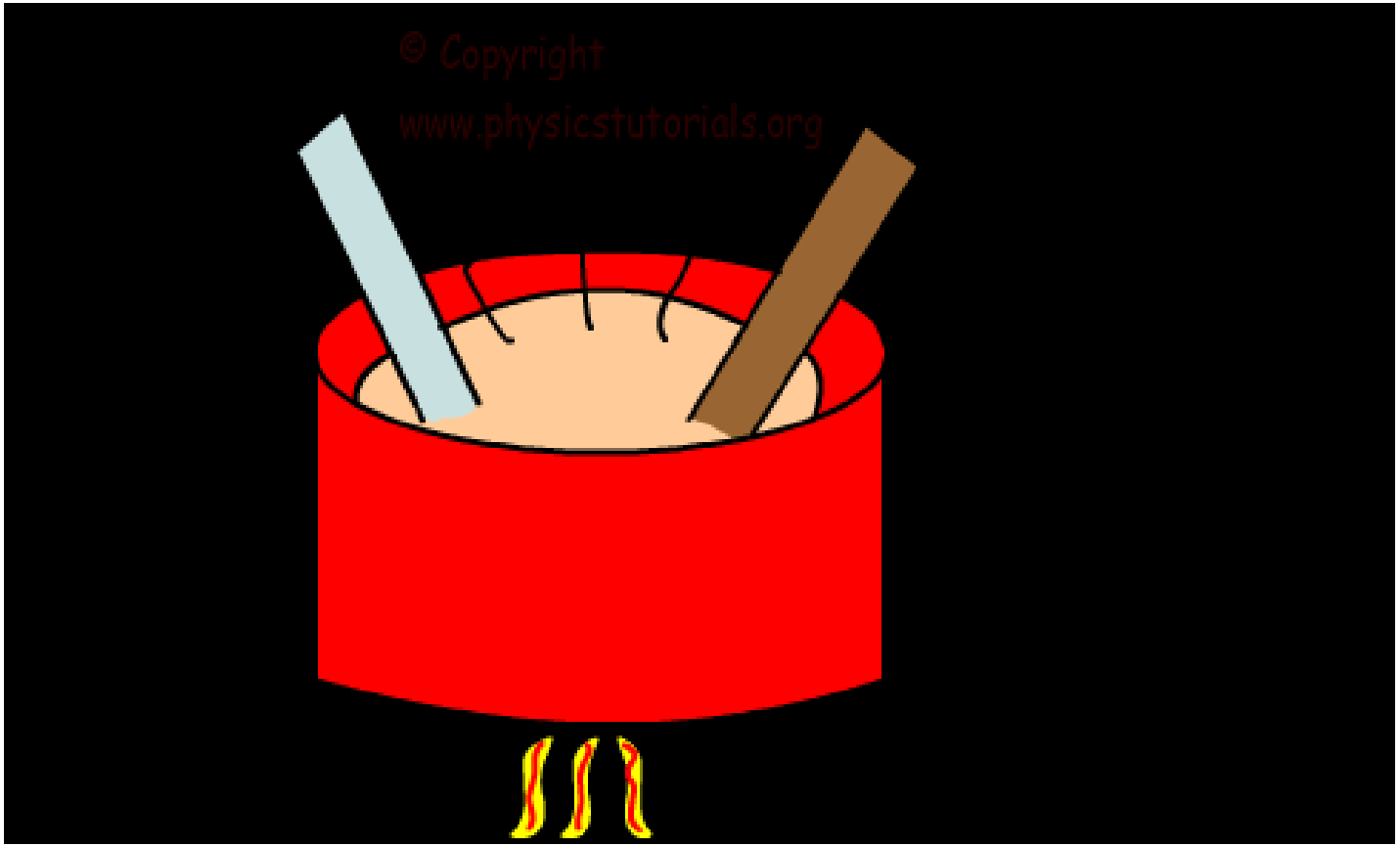
- Work is energy, and the unit is the Joule.
- Joule = N·m
- = kg·m/s2·m
- = kg·m2/s2

Definitions

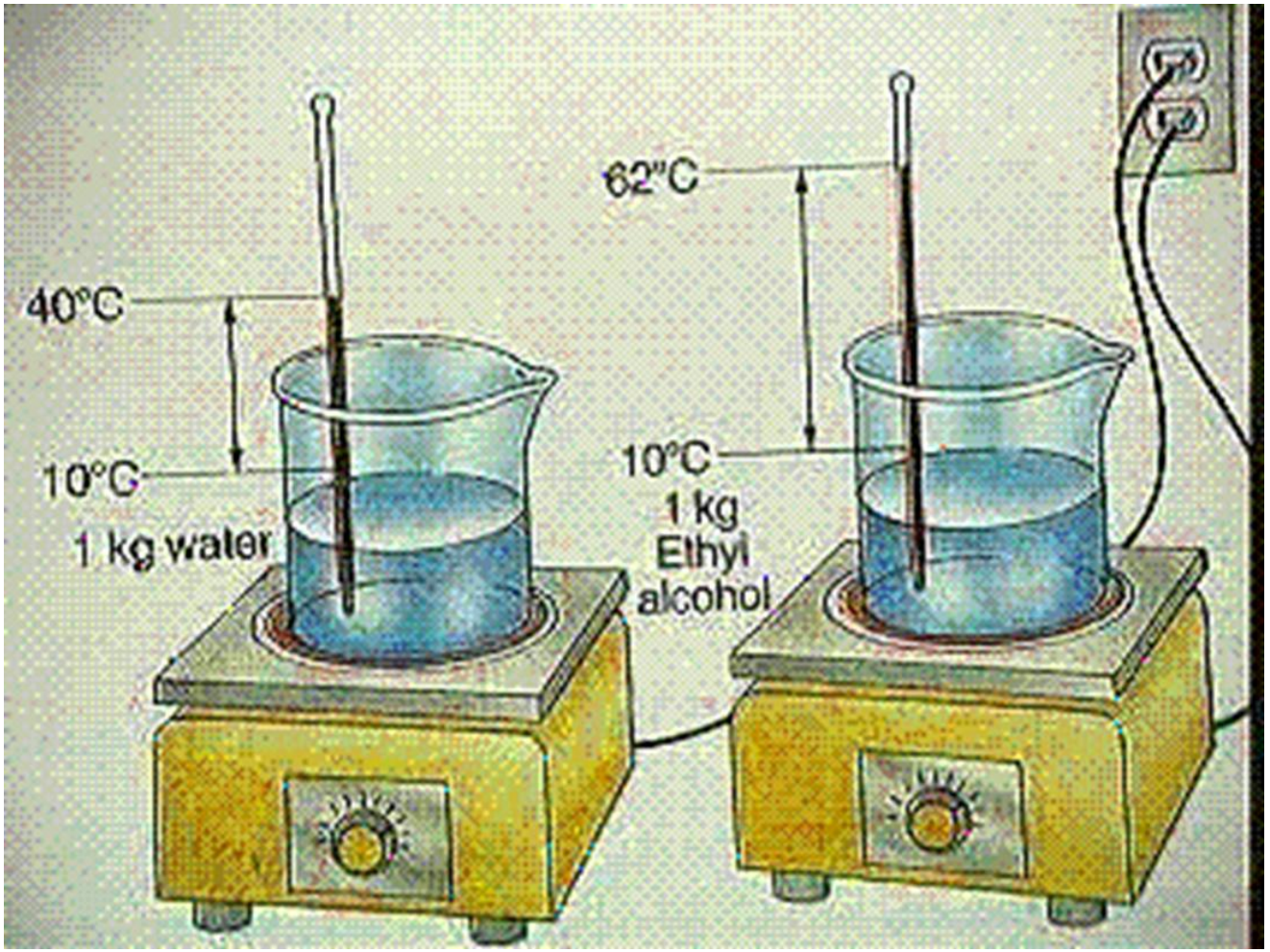
Temperature

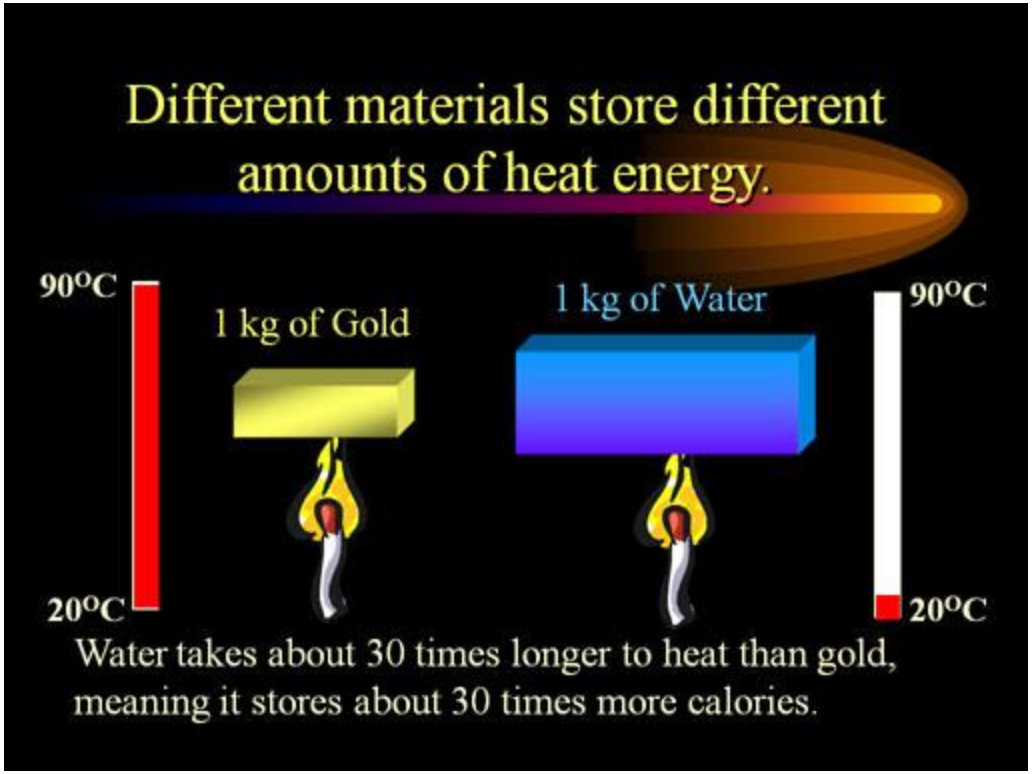
A property of an object which determines the direction of **Heat Flow** when the object is placed in thermal contact with another object.

Heating is transfer of energy from a hotter body to a colder one



Same amount of heat energy yielding different temperatures




Different materials store different amounts of heat energy.
90°C
20°C
1 kg of Gold
1 kg of Water
90°C
20°C
Water takes about 30 times longer to heat than gold, meaning it stores about 30 times more calories.

The heat energy needed to raise the temperature of an object by 1 K is called the HEAT CAPACITY of the object.

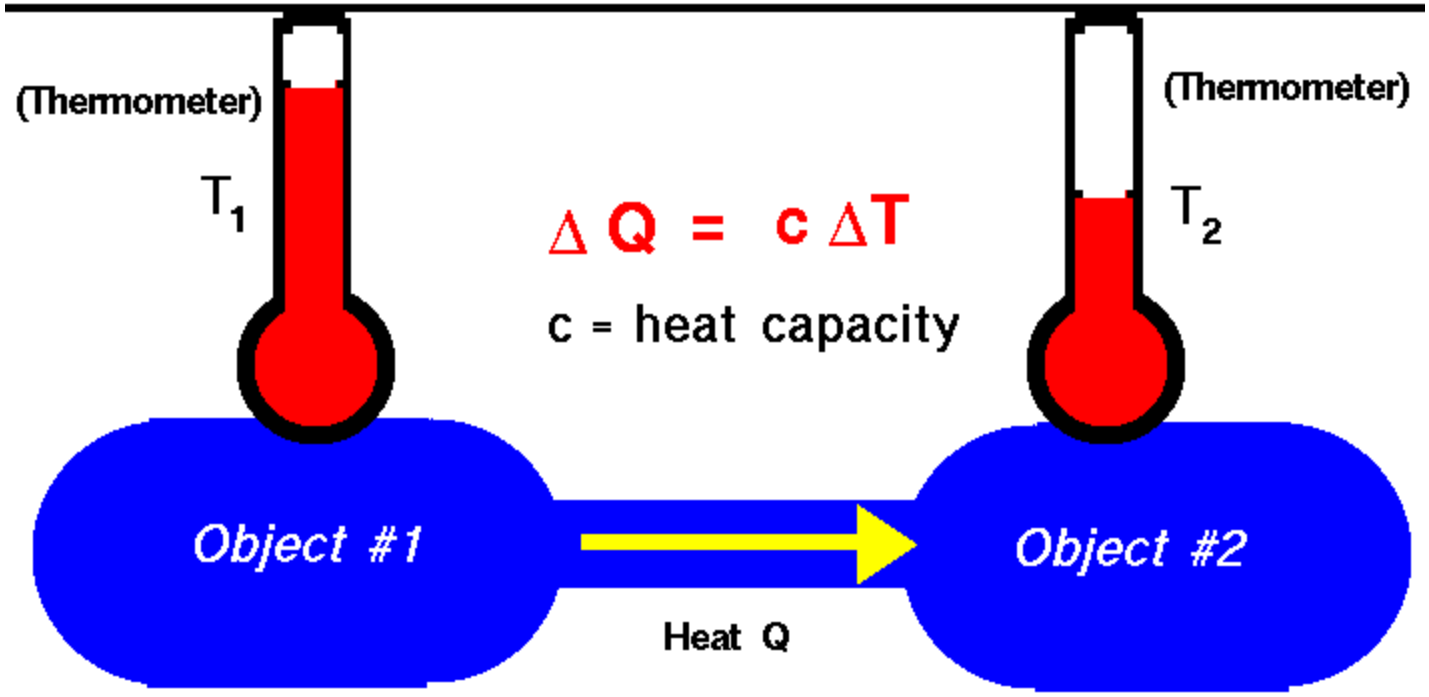
The SPECIFIC HEAT CAPACITY of a substance is the heat needed to raise the temperature of 1 Kg of the substance by 1 K (or by 1 oC)

$$Q = mc\theta$$

m = mass	(kg)
c = specific heat capacity	(J kg^{-1} $^oC^{-1}$)
θ = temperature change	(^oC)

Heat Transfer

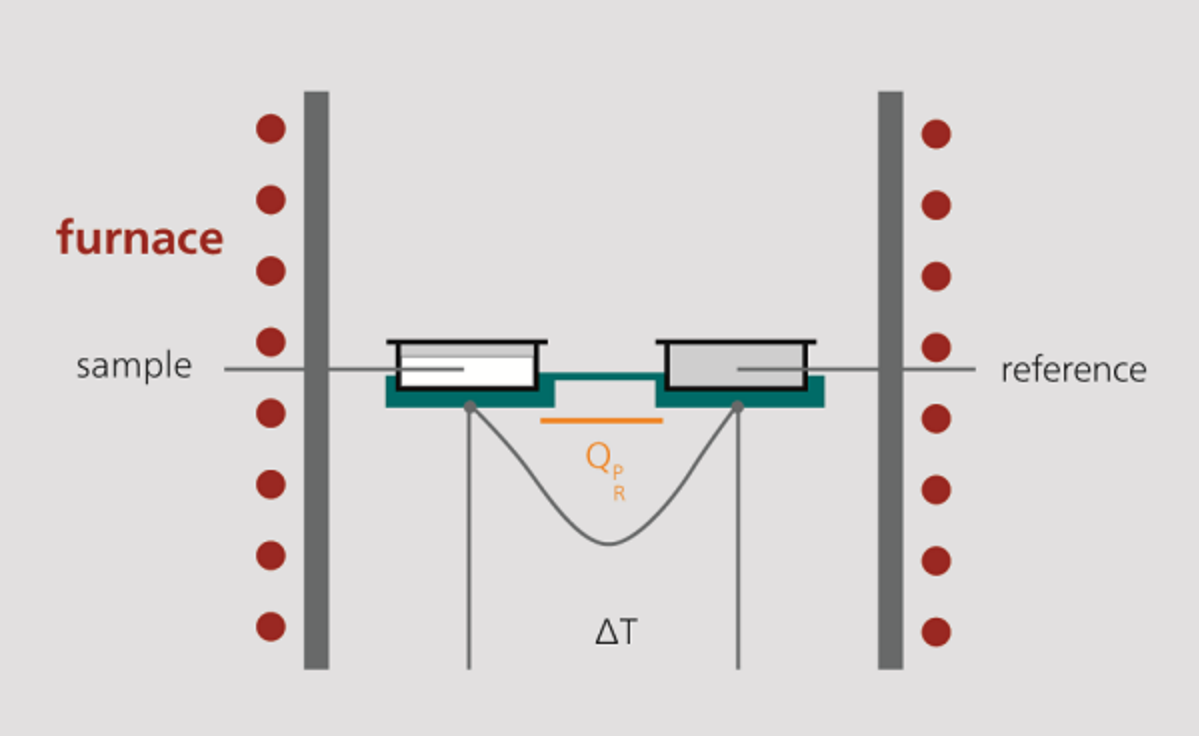
Glenn Research Center



In the process of reaching thermodynamic equilibrium, heat is transferred from the warmer object to the cooler object. At thermodynamic equilibrium heat transfer is zero.

Definition

Differential Scanning Calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature (Wikipedia).


furnace
sample
reference
Q_{P_R}
ΔT

Heat Flow

Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic

Exothermic Reaction

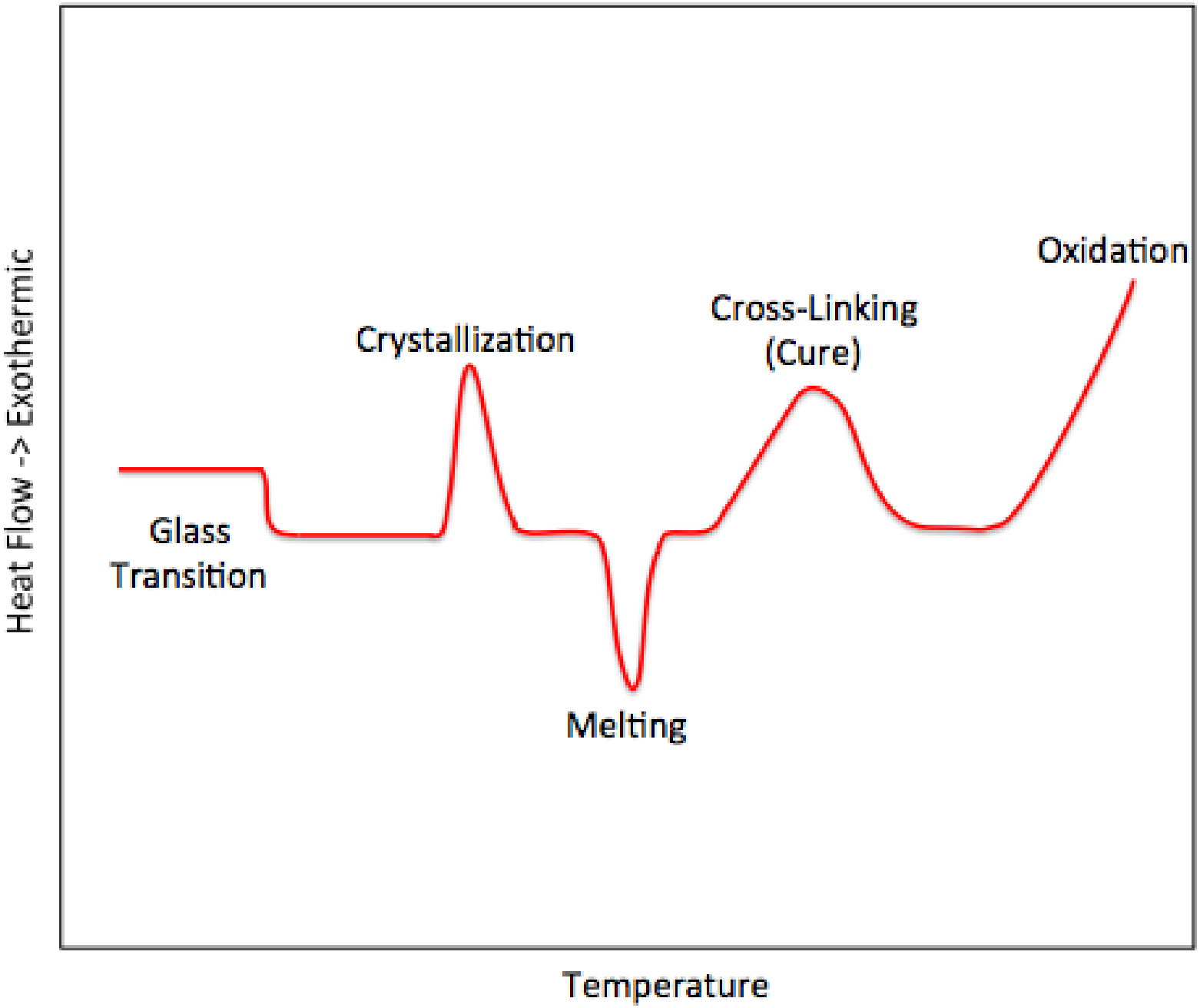
sugar and concentrated sulfuric acid

$C_{12}H_{22}O_{11}$ Dehydrate $12C(s) + 11H_2O(l)$ Oxidise CO_2, SO_2

Endothermic Reaction

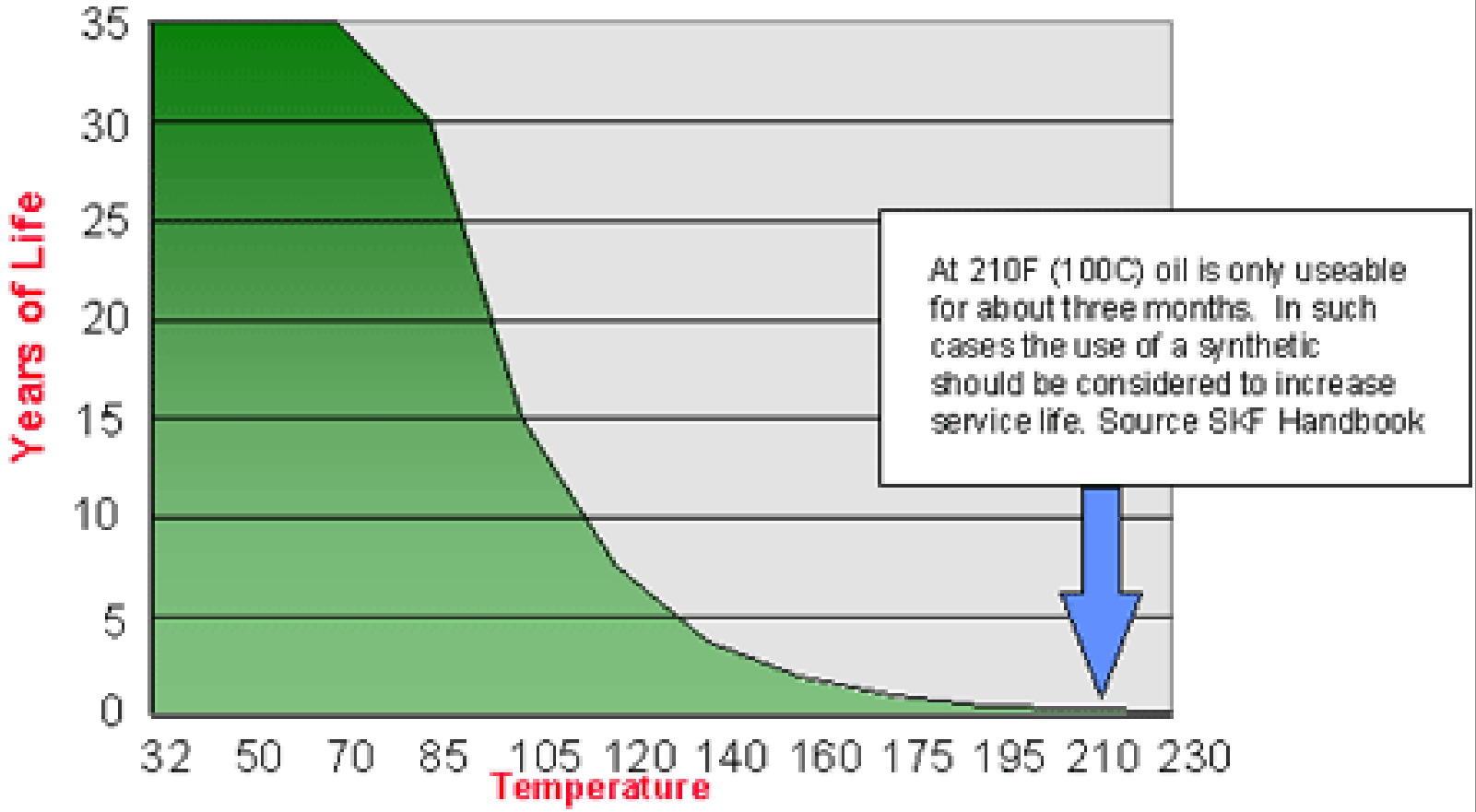
Barium Hydroxide and Ammonium Nitrate

$Ba(OH)2{\cdot}8H2O(s) + 2\ NH4NO3(s) \rightarrow 2\ NH3(g) + Ba2+(aq) + 2\ NO3-(aq) + 10\ H2O(l)$


Heat Flow -> Exothermic
Oxidation
Cross-Linking
(Cure)
Crystallization
Glass
Transition
Melting
Temperature

The Effect of Temperature

As a rule of thumb service life of mineral oils specified for 30 years @ 85 F, 15 years @ 105 F. The oils life is halved for each 18 F (10 C) increase in temperature

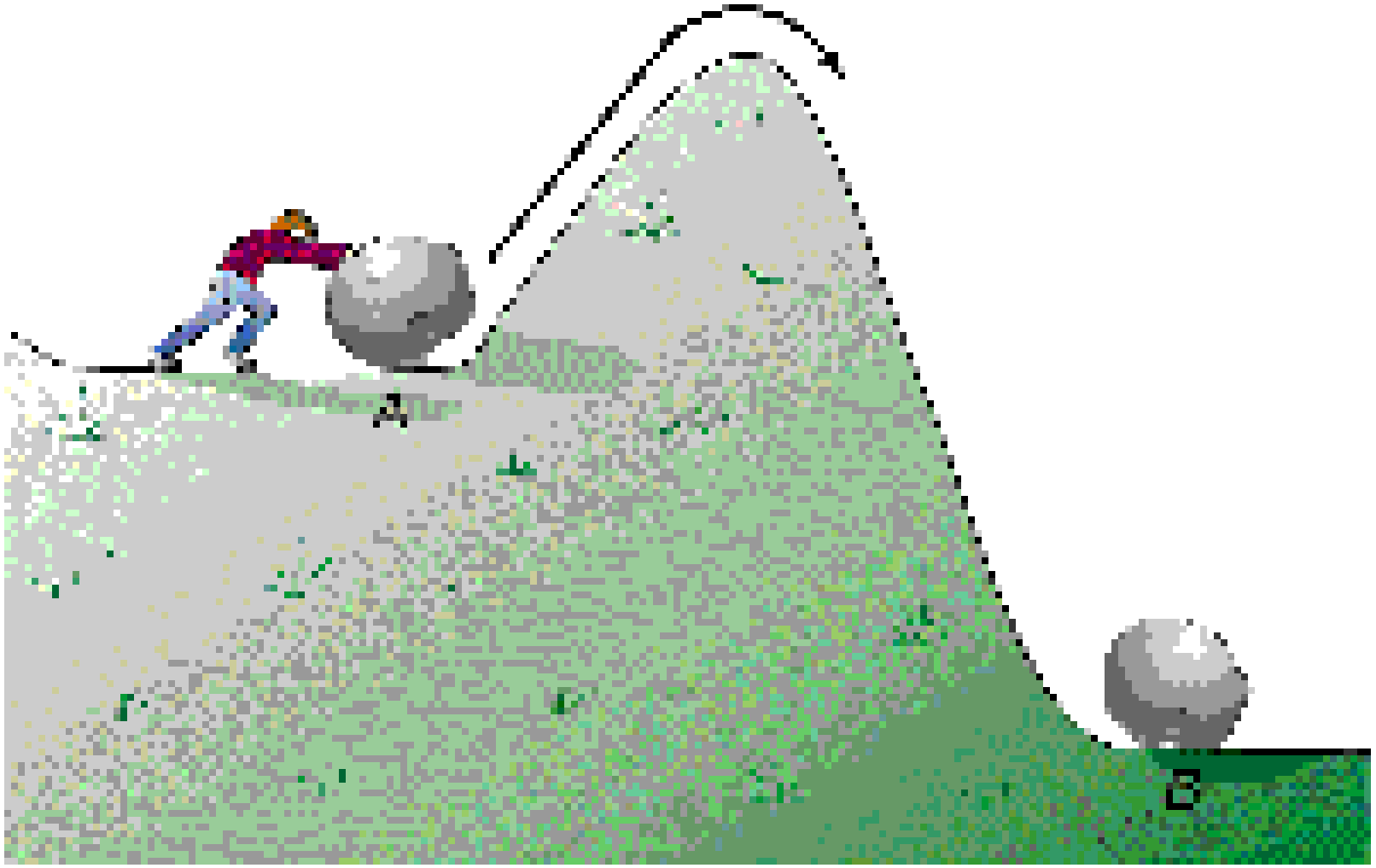


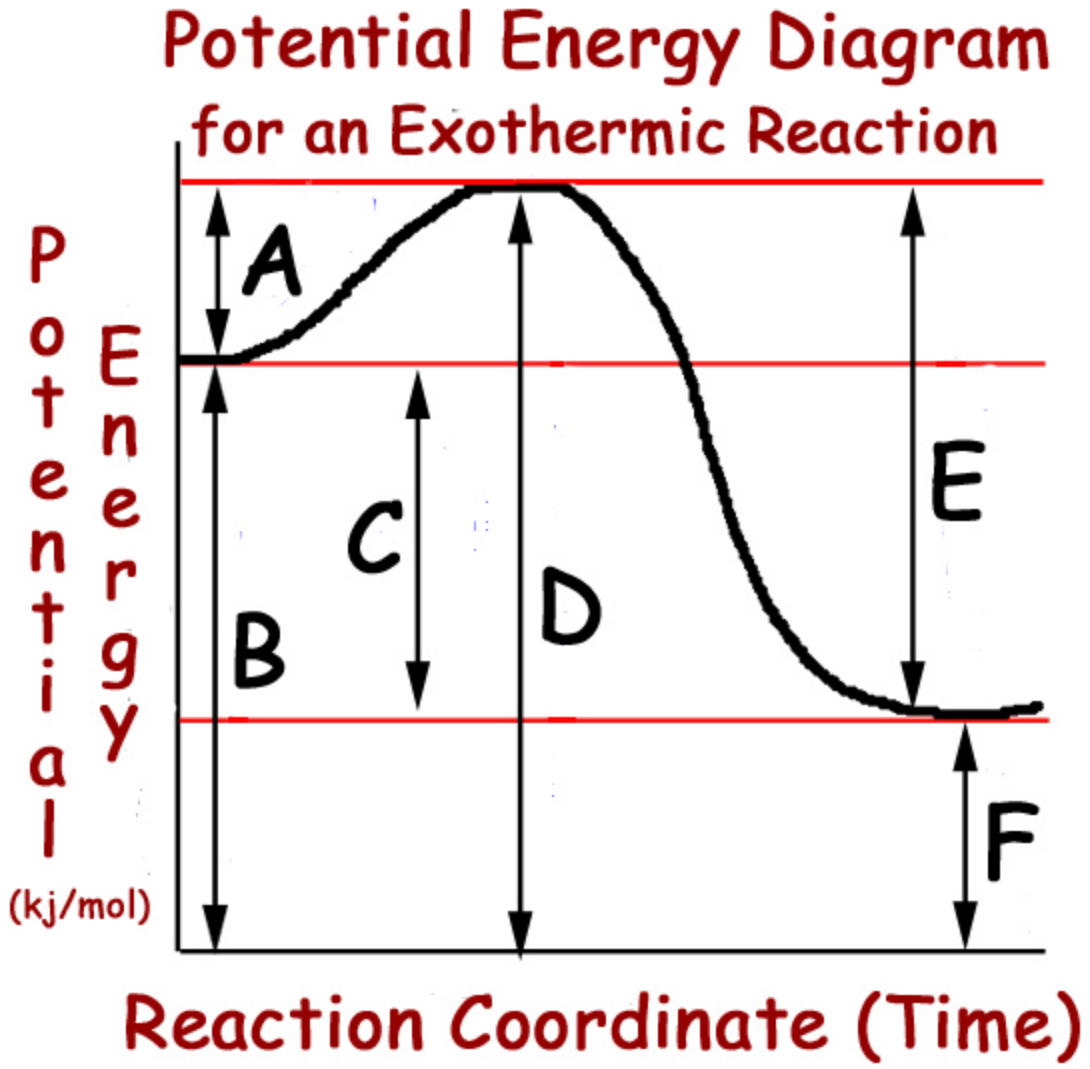
NETZSCH

Tzero® PRESSURE
DSC CELL
TA

PDSC Work Plan Outcomes

- Temperature Calibration (NBS Tin SRM)
- Temperature Stability (< +/- 0.5 C at 200 C for 900 min)
- Effect of Sample Size: (thin disc: 83 min, powder: 61 min)
- Repeatability (isothermal 227 C: +/- 0.5 C)
- Effect of Pressure (69 min@500 psi, 56 min@600 psi)
- Effect of Temperature (69 min @ 227 C, 201 min @ 207 C, 648 min @ 187 C)
- Effect of Purge Rate (69 min @ 20 cc/min, 68 min@ 0 cc/min)


A
B



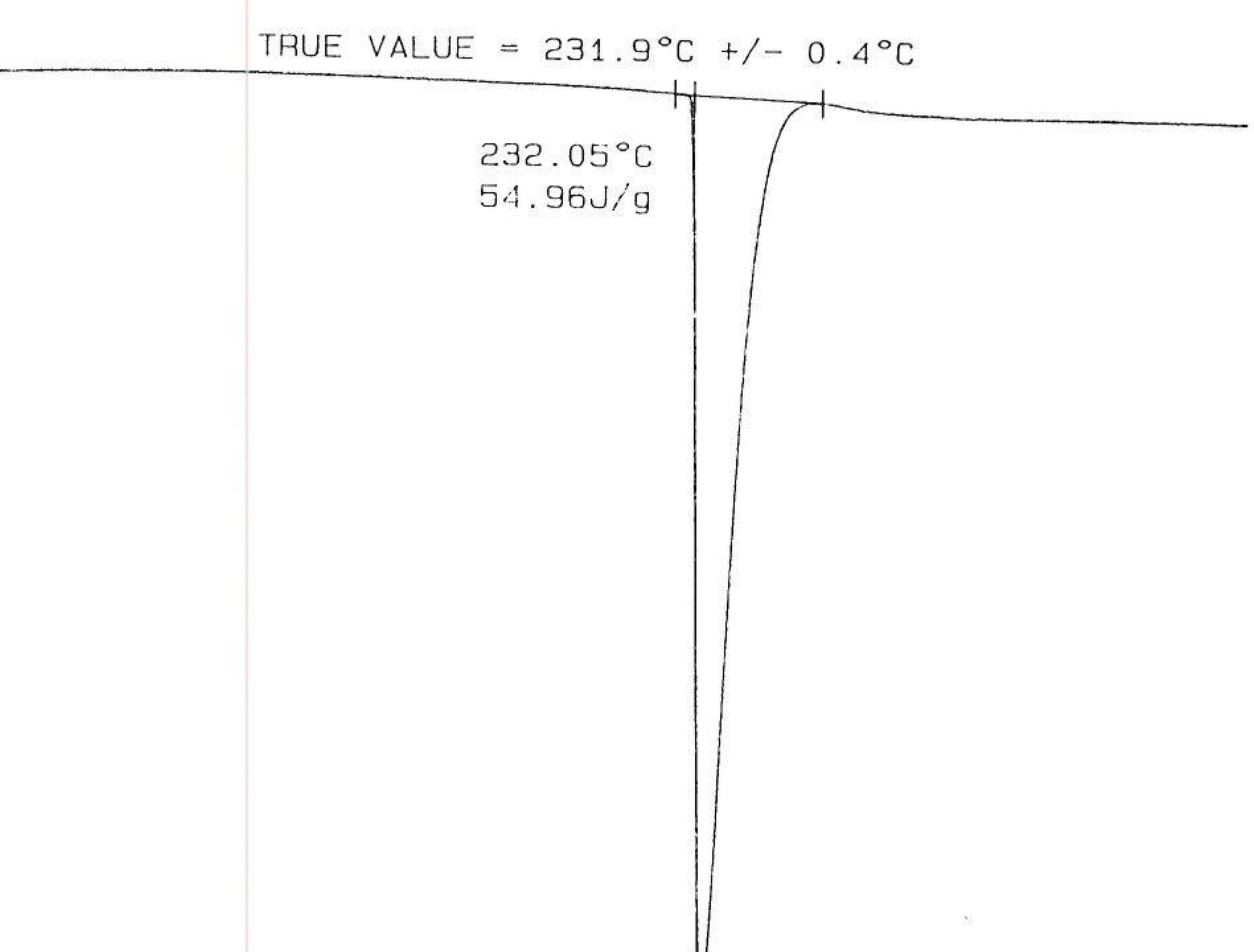
A: Activation Energy
B: Potential Energy of the Reactants
C: delta H
D: Activated Complex
E: Activation Energy of Reverse Reaction
F: Potential Energy of the Products

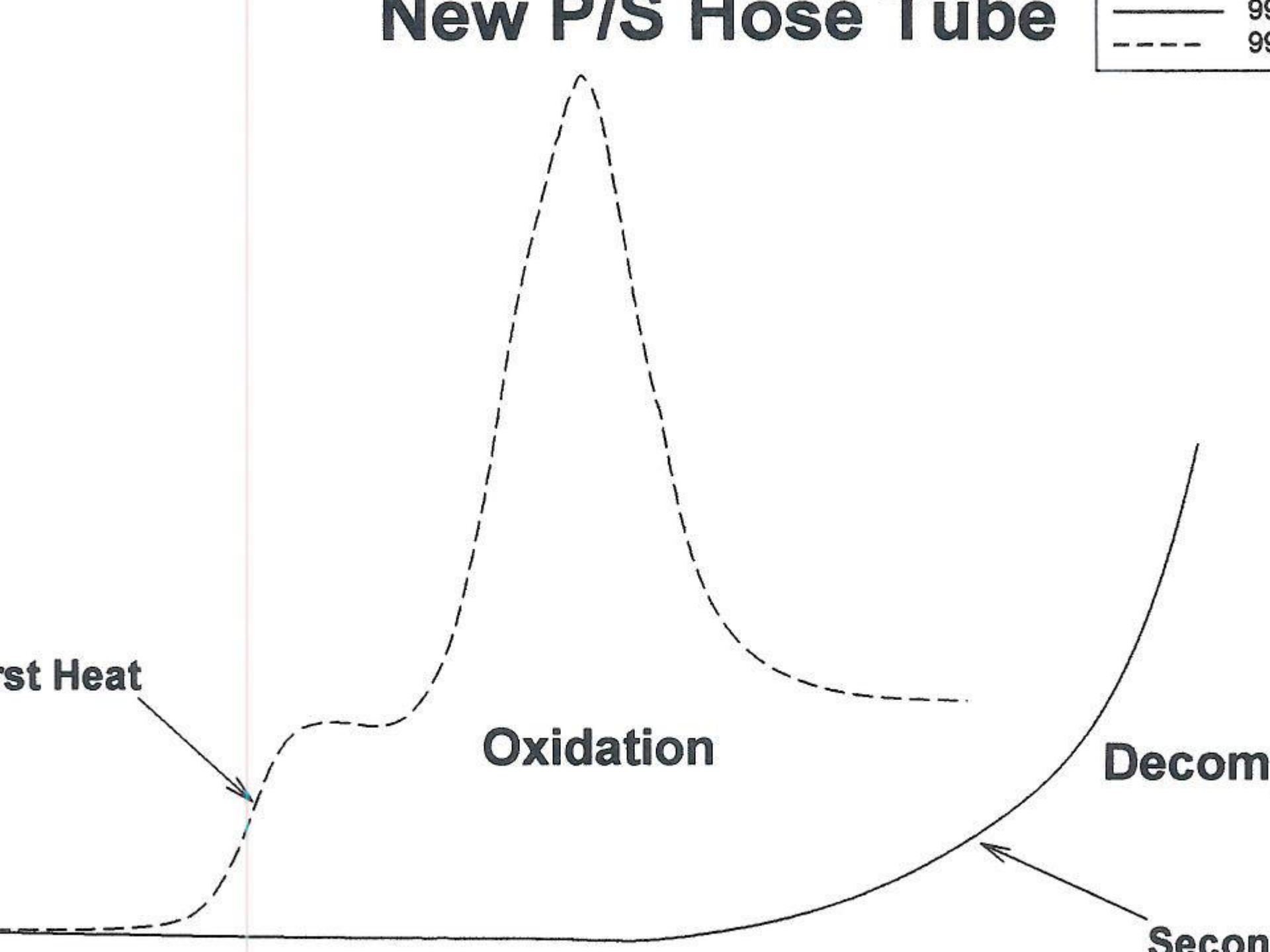
$$lnK = lnA - \frac{E_a}{RT}$$

$$logK = logA - \frac{E_a}{2.303\ RT}$$

Where

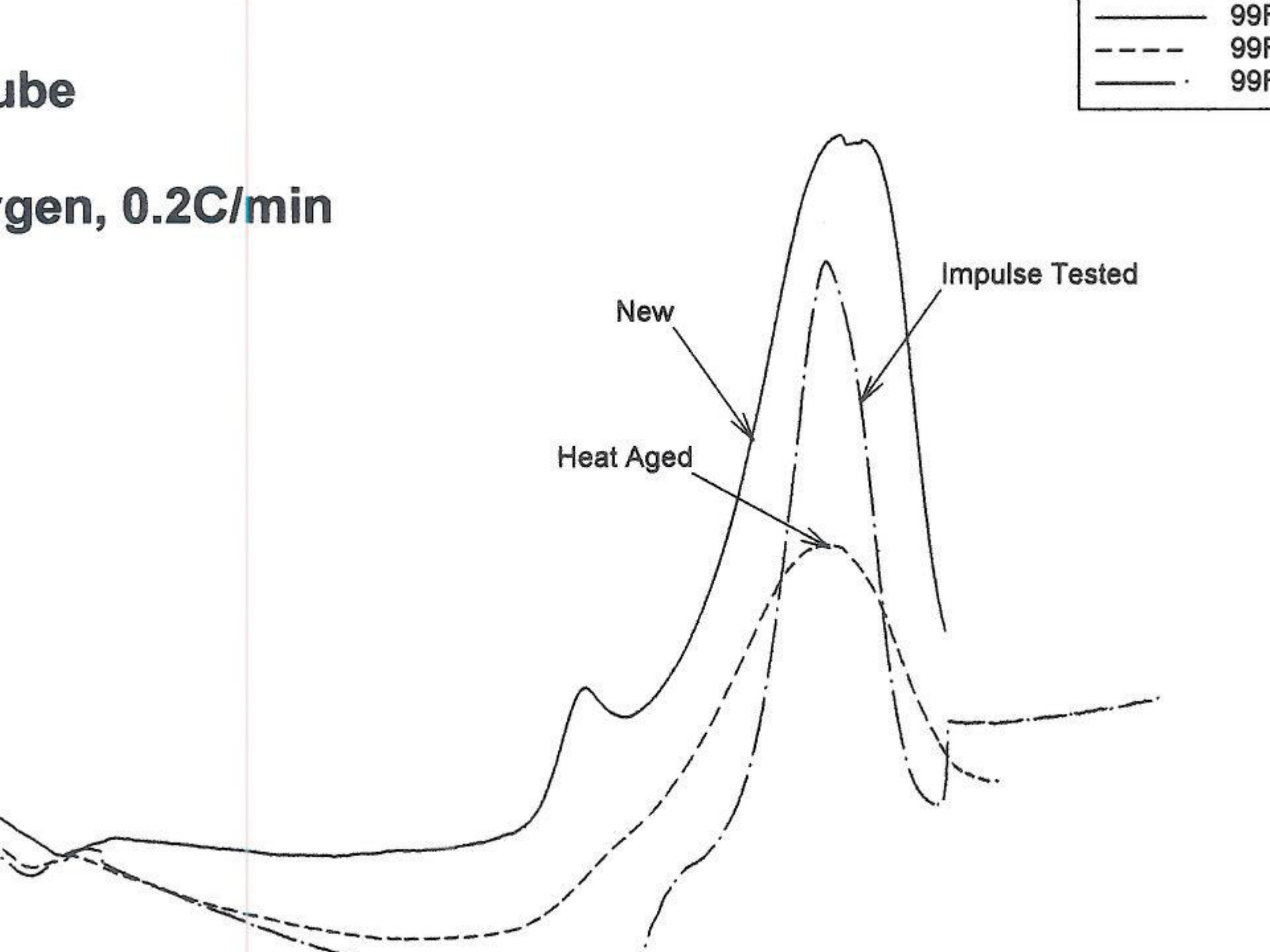
k is the rate constant
A is called the frequency factor
Ea is the activation energy
R is gas constant (8.314 x 10-3 kJ mol-1K-1)
T is absolute temperature
Thus plot of lnK versus 1/T yields a straight line whose slope which is negative is equal to -Ea/R.


TRUE VALUE = 231.9°C +/- 0.4°C
232.05°C
54.96J/g

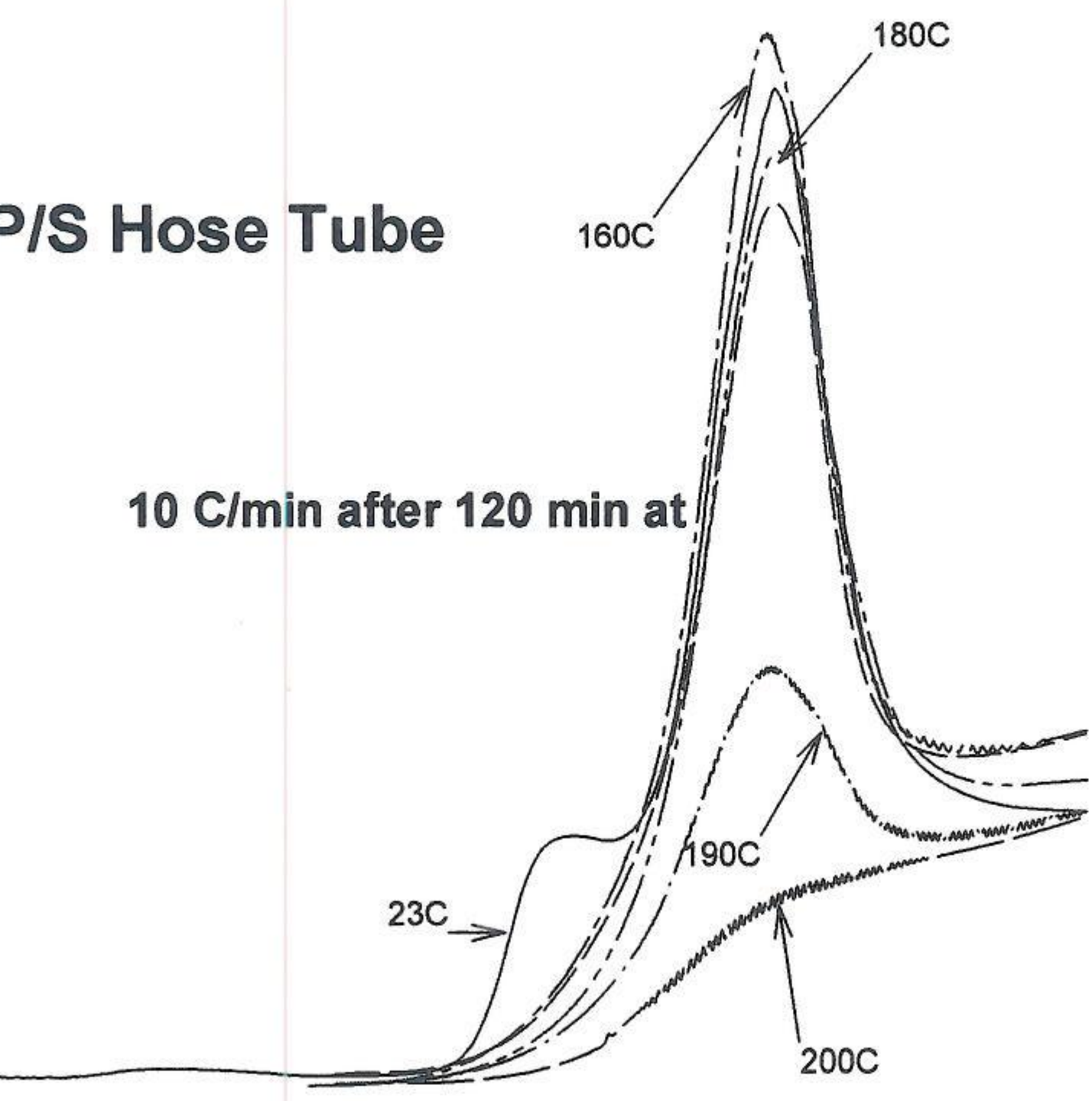

New P/S Hose Tube
rst Heat
Oxidation
Decom
Secon

ube

gen, 0.2C/min



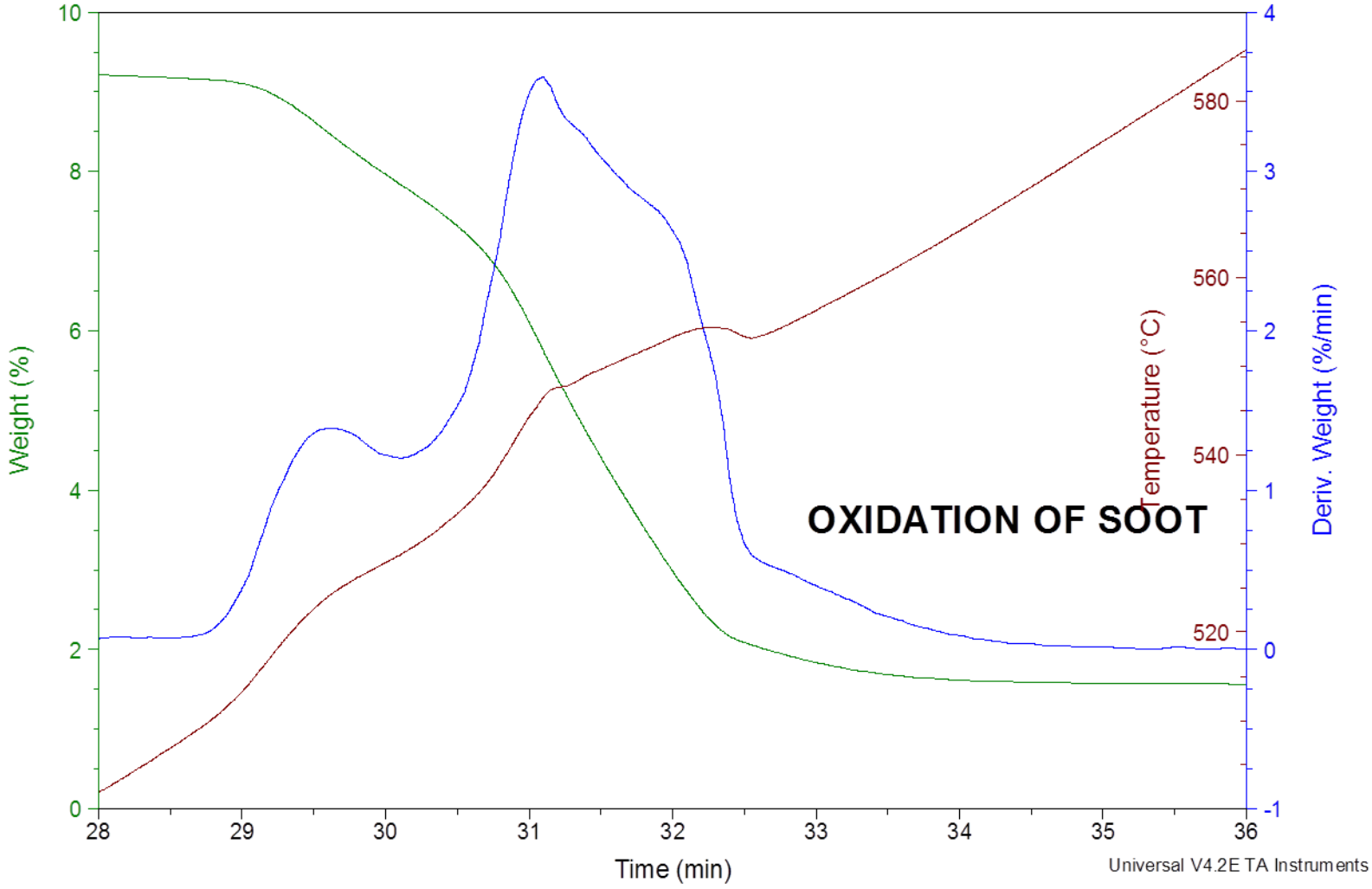
P/S Hose Tube



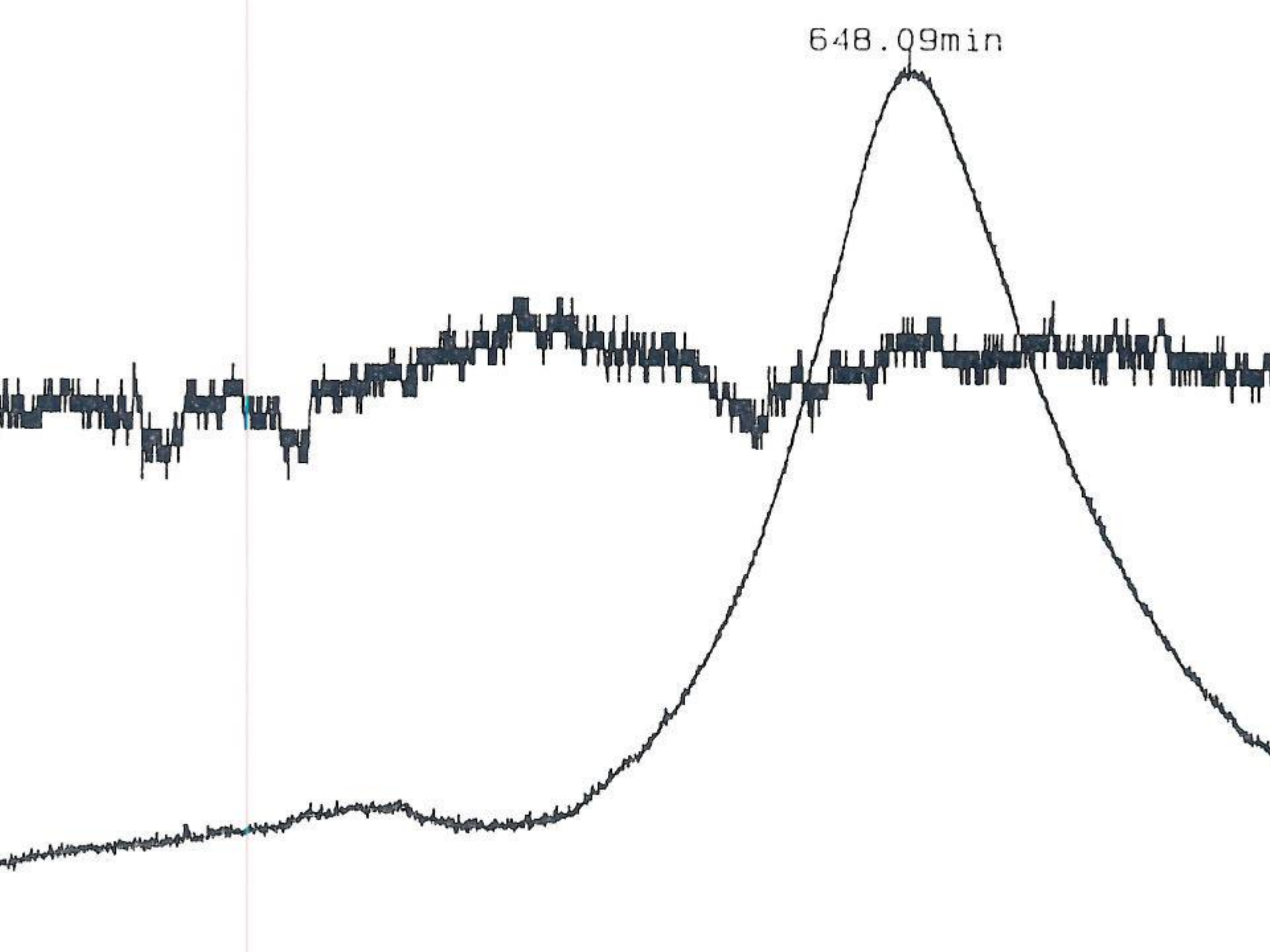
Sample: S060517J BLACK OIL
Size: 70.5650 mg
Method: NEW OIL PROGRAM 20/10
Comment: NITROGEN, THEN AIR, 70 CC/MIN

TGA

File: A:\06S21.07
Operator: POLYTHERM TESTING LAB
Run Date: 20-May-2006 10:56

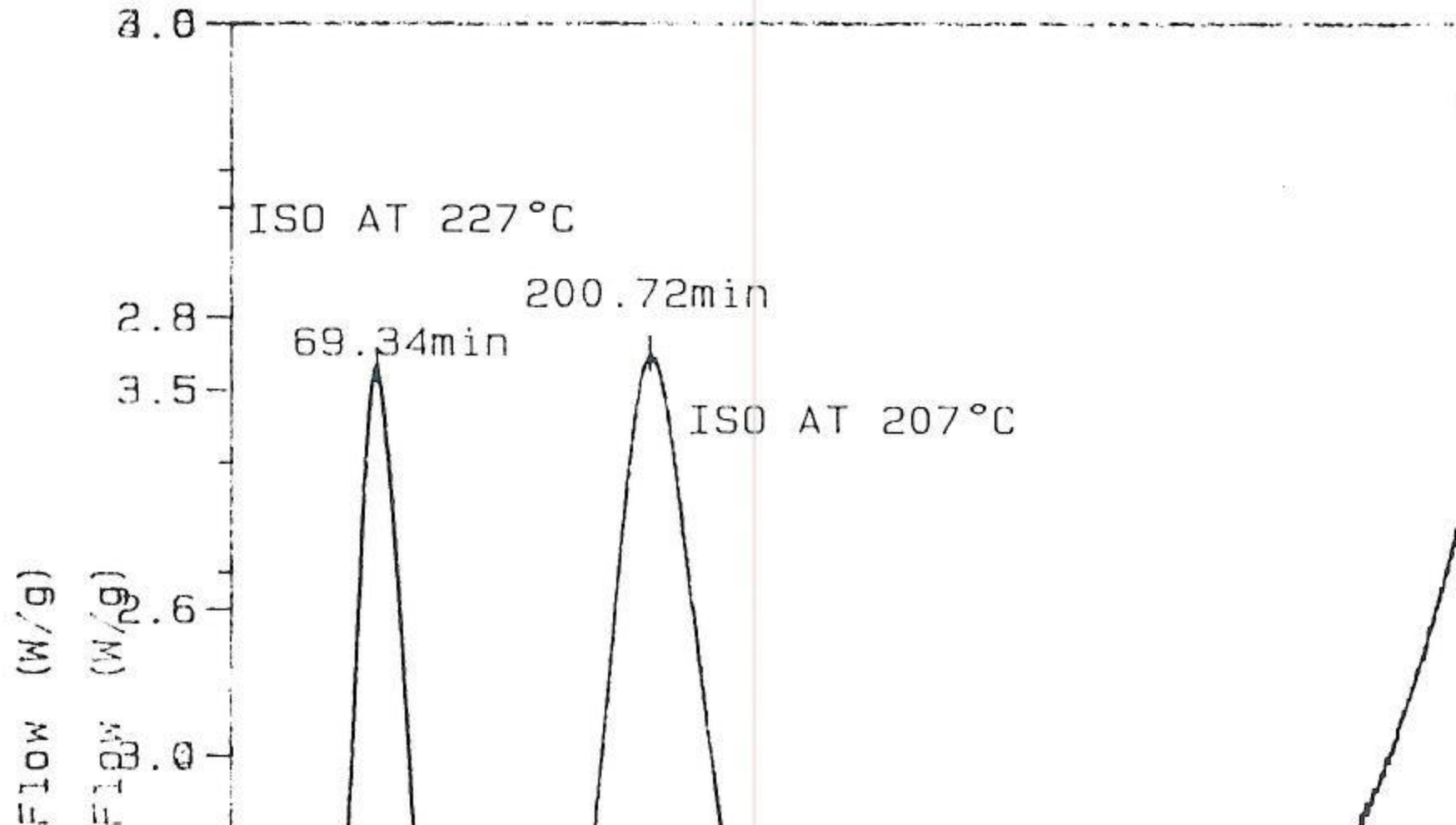


Universal V4.2E TA Instruments


648.09min

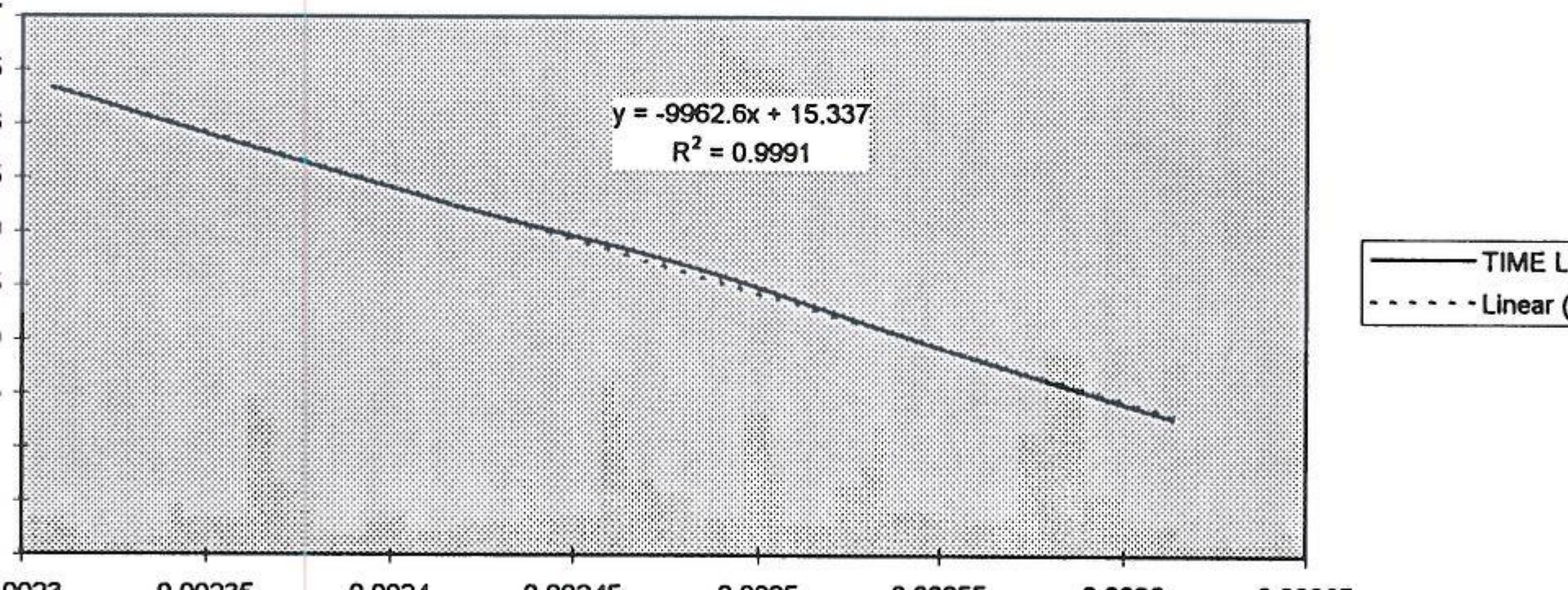
Sample: FORD PROJECT-EXHAUST ISOLATOR
Size: 0.9800 mg
Method: PDSC, ISOAT@227°C
Comment: AIR (~50 cc/min), 500 psi PDSC (CLUMPED CH

DSC

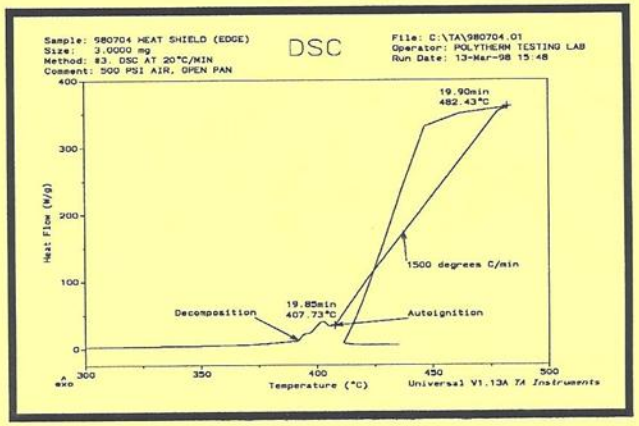


105.9		0.002417795	-8.756839815					
185.5		0.00248139	-9.317399444					
377.34		0.002545825	-10.0274912					
763.6		0.002613696	-10.73238865					

PLOT OF DATA FROM PDSC



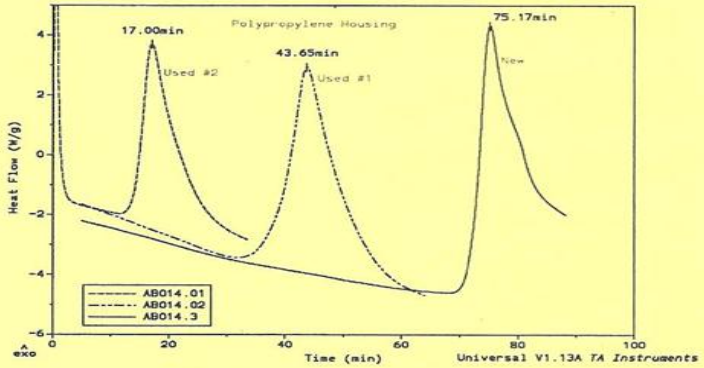
Oxidative Stability of Plastics, Elastomers, Lubricants and other Organic Compounds by PDSC (Pressure Differential Scanning Calorimetry)



Oxidative Stability by PDSC[1]

Certain compounds degrade when heated. If the heating is done in air or oxygen, most materials oxidize. Under certain conditions, some materials autoignite, releasing large quantities of heat energy in a fraction of a second (see chart on the cover page). Effectiveness of fire retardant formulations (amounts, types, etc.) can be evaluated by this technique.

Under standard temperature and pressure, polymers and other organic materials undergo slow oxidation in air. Compounders retard material oxidation by adding antioxidants to their formulations. Materials will retain acceptable mechanical properties as long as levels of antioxidants are adequate to prevent polymer chain breakdown by oxidation. Using high temperature and pressure, PDSC can help determine antioxidant depletion rates under service or other accelerated aging conditions.

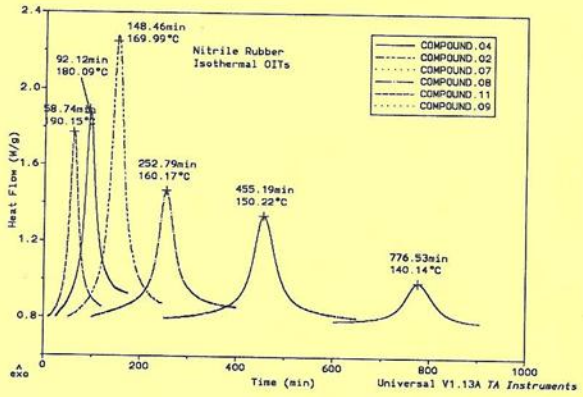


Above is a composite chart showing the Oxidation Induction Times (OIT) of a stabilized talc-filled polypropylene before and after use. By comparing OITs against service duration (miles, cycles, years, etc.), product useful life predictions have been made for several types of materials, including greases, engine oils, and transmission fluids.

[1]For Test Method Information, see ASTM E-537

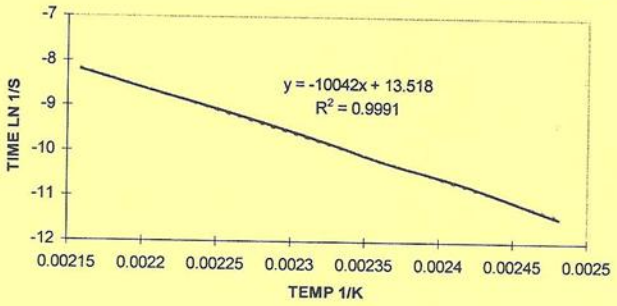
Polytherm Testing Laboratory, 1032-O Crooks Road, Clawson, MI 48017

PDSC can be conducted at different heating rates or isothermally at one or more temperatures. For example, the polypropylene experiments were all performed at 175°C. Testing isothermally at various temperatures can help characterize the overall oxidative stability of a material.



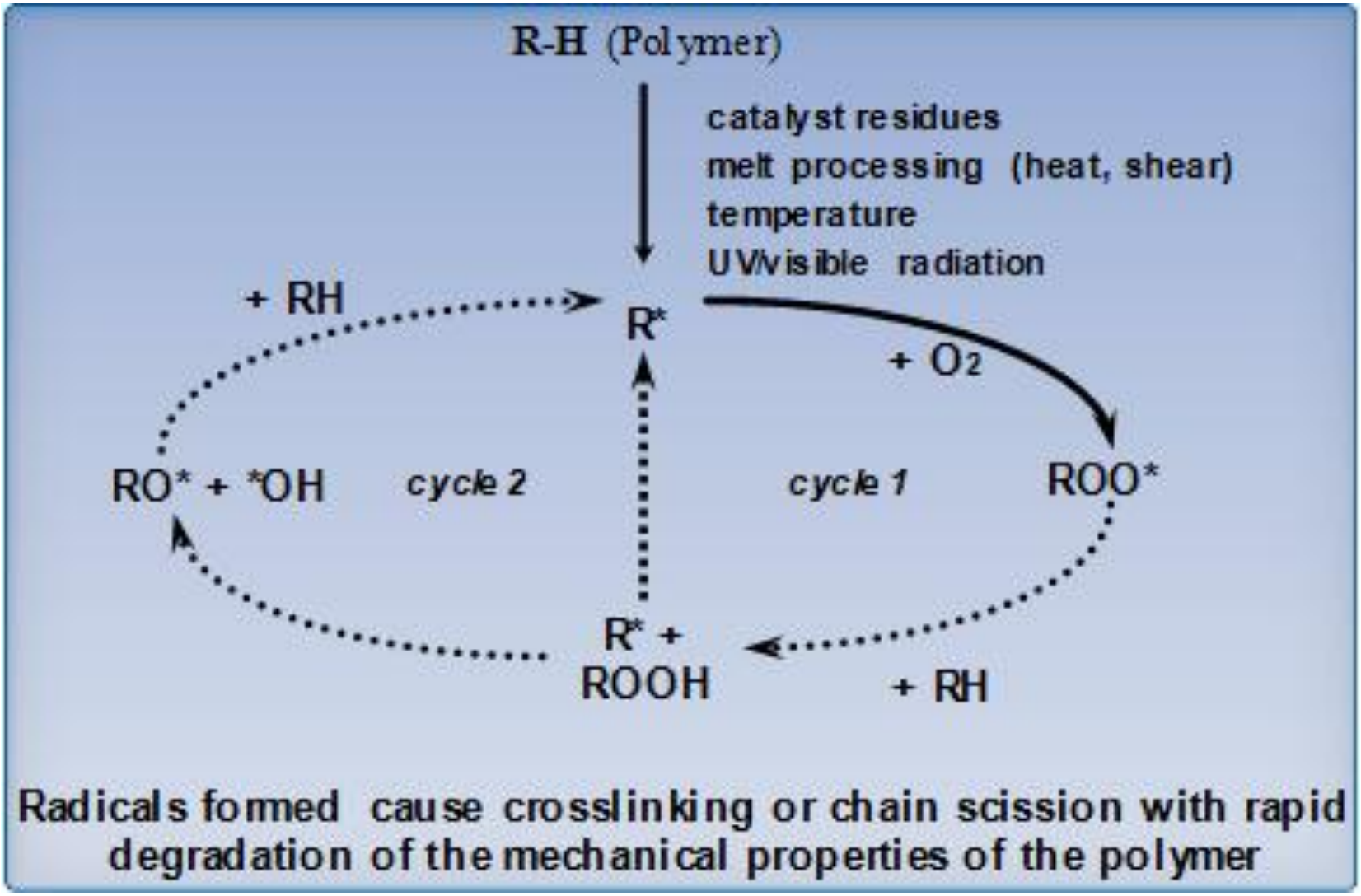
The above chart is an overlay of six isothermal runs of a Nitrile Butadiene Rubber (a seventh, at 130°C, with an OIT of 1553 minutes, is not shown on purpose). From these times and temperatures, the chart below is generated.

From the slope, the Activation Energy (84 kJ/mole) is obtained for this NBR.



Please call or write for additional information.

Polymer Oxidation Cycle



Polymer Antioxidants

- ANOX®, LOWINOX®, WESTON® and NAUGARD® phenolic antioxidants
- NAUGARD®, OCTAMINE® and FLEXAMINE® aminic antioxidants
- DURAZONE®, FLEXZONE® and NOVAZONE® antiozonants
- LOWINOX® and NAUGARD® metal deactivators
- ALKANOX®, WESTON® and ULTRANOX® phosphite antioxidants
- NAUGARD® thioester antioxidants
- GENOX® amine oxide antioxidants

Where PDSC has been Useful

- Activation Energy Determinations for Elastomers and Plastics
- KTP E-Coat Oven Fire Investigations
- Grease Blend Optimization (L. Mastro)
- Polymeric Part Useful Life Predictions
- Underhood Part Fire Investigations
- Power Steering Fluid Oxidative Stability
- Polymer Failure Analysis
- Additive Package Depletion Studies

Published PDSC Test Procedures

- ASTM D3895 Oxidative Induction Times of Polyolefins by DSC
- ASTM D5483 Oxidative Induction Time of Lubricating Greases by PDSC
- ASTM D6186 Oxidative Induction Times of Lubricating Oils by PDSC
- ASTM E1858 Oxidation Induction Times of Hydrocarbons by DSC
- ASTM E2009 Oxidation Onset Temperature of Hydrocarbons by DSC
- ASTM E2046 Reaction Induction Time by Thermal Analysis
- ASTM E2070 Kinetic Parameters by DSC Using Isothermal Methods
- ISO 11357-6:2008 Plastics -- Differential scanning calorimetry (DSC) -- Part 6: Determination of oxidation induction time (isothermal OIT) and oxidation induction temperature (dynamic OIT)

Summary

- PDSC is an accelerated calorimetric technique
- Still considered new (on market since early 1960s)
- Can obviate the need of other, often tedious, long-term aging tests
- More and more industries are using this technique to make useful life predictions

Questions

(Operating Limits, Safety, Price, etc.)