# New Developments in Coal Physics

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# Physics

- A subject that induces fear and loathing in students and most of their teachers. Synonyms include incomprehensible, waste of money, and mind-numbing.

  — *Leon Lederman*

# In the beginning was Larsen…

- Native coals are strained.
- Solvent swelling relieves the strain. Coal structure rearranges to a new structure of lower free energy and with greater non-covalent associations.
- This change is irreversible. After the first swelling, the second, third… swellings are essentially identical.

See Larsen et al., *Energy Fuels* **1997**, *11*, 998

# The solvent swelling effect

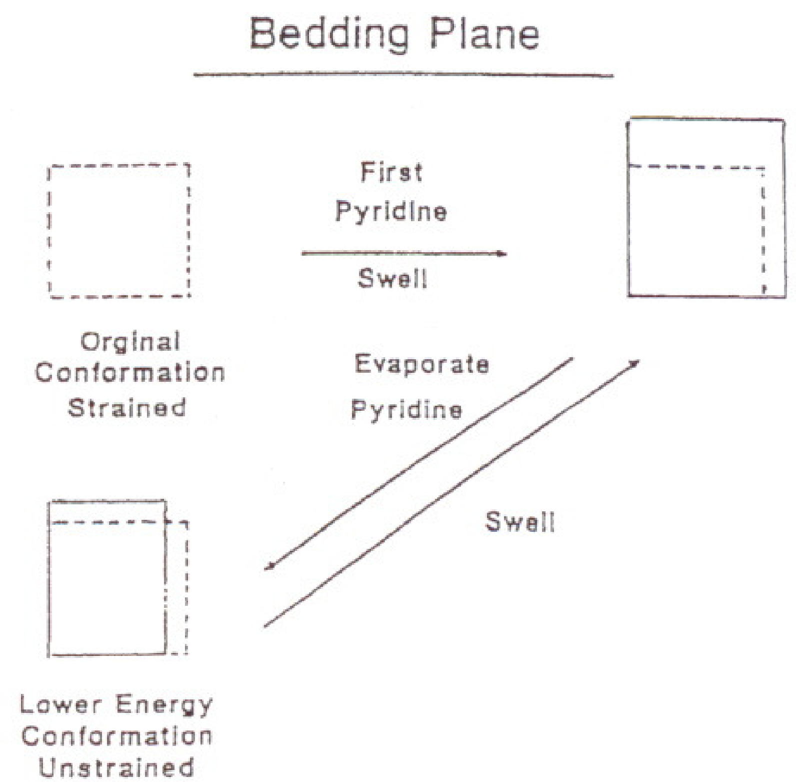



**Figure 1.** Diagram of coal one-time irreversible swelling.

# Dynamic mechanical analysis

- DMA applies an oscillating force to a sample and measures the material's response to that force.
- DMA results can be related to the relaxation of polymer chains or changes in the free volume of the polymer.

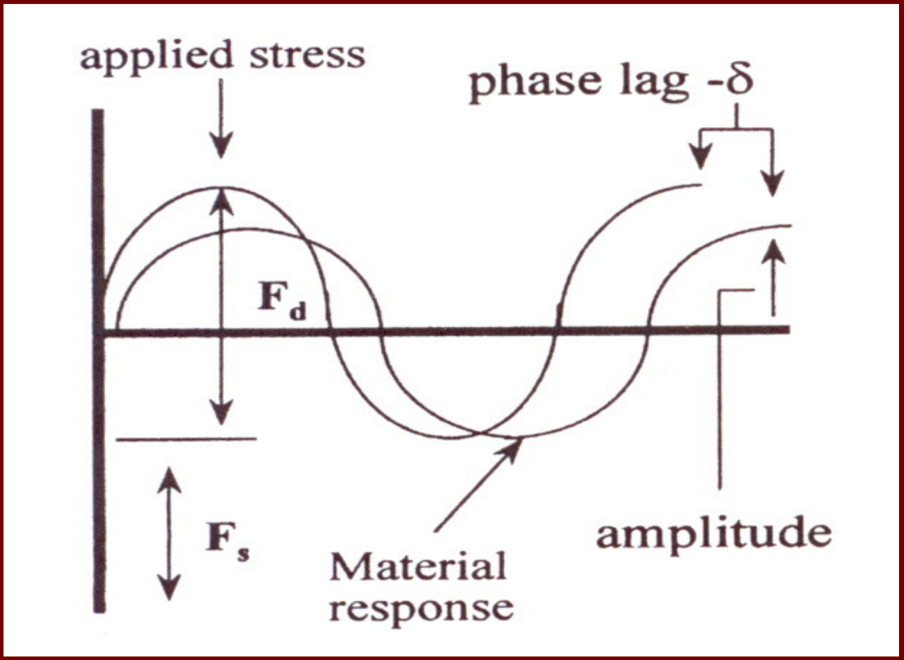
See, e.g., Menard, *Dynamic Mechanical Analysis*, CRC Press, 1999.

# Examples of DMA measurements

- *Viscosity:* resistance to flow
- *Modulus:* the stiffness of the material
- *Damping:* ability of the structure to lose energy (usually as heat)
- *Elasticity:* ability to recover from deformation

# The DMA phase lag

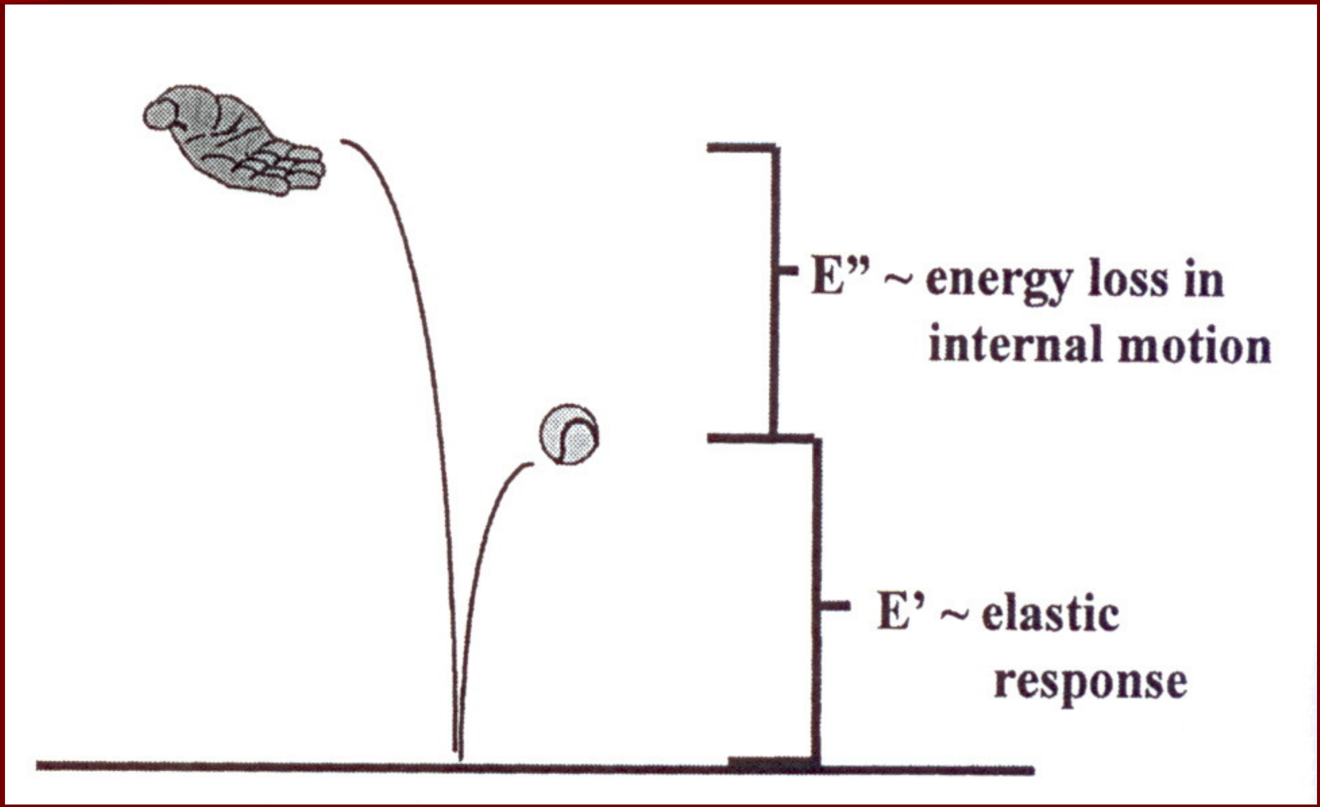
- DMA applies an oscillatory stress, σ, which induces a strain, γ.
- The response of the material to σ is often characterized by a phase lag, δ.



# Relating phase lag to materials characteristics

- For a perfectly elastic material, $\delta = 0$, i.e., there is no phase lag (an “in-phase” response).
- For a purely viscous material, $\delta = \pi/2$, a perfectly out-of-phase lag of 90°.
- Viscoelastic materials fall between these extremes, i.e., $0 < \delta < \pi/2$.
- As luck would have it, coals and most polymers are viscoelastic.

# Storage and loss of energy in a stressed material



# The storage modulus, E'

- E' is a measure of how elastic a material is: stress/deformation, or $\sigma/\varepsilon$.
- Ideally, E' would be equivalent to Young's modulus.
- In the baseball analogy, E' is the amount of energy the ball gives back, i.e., how high it bounces.
- $E' = (\sigma/\varepsilon)\cos\delta$

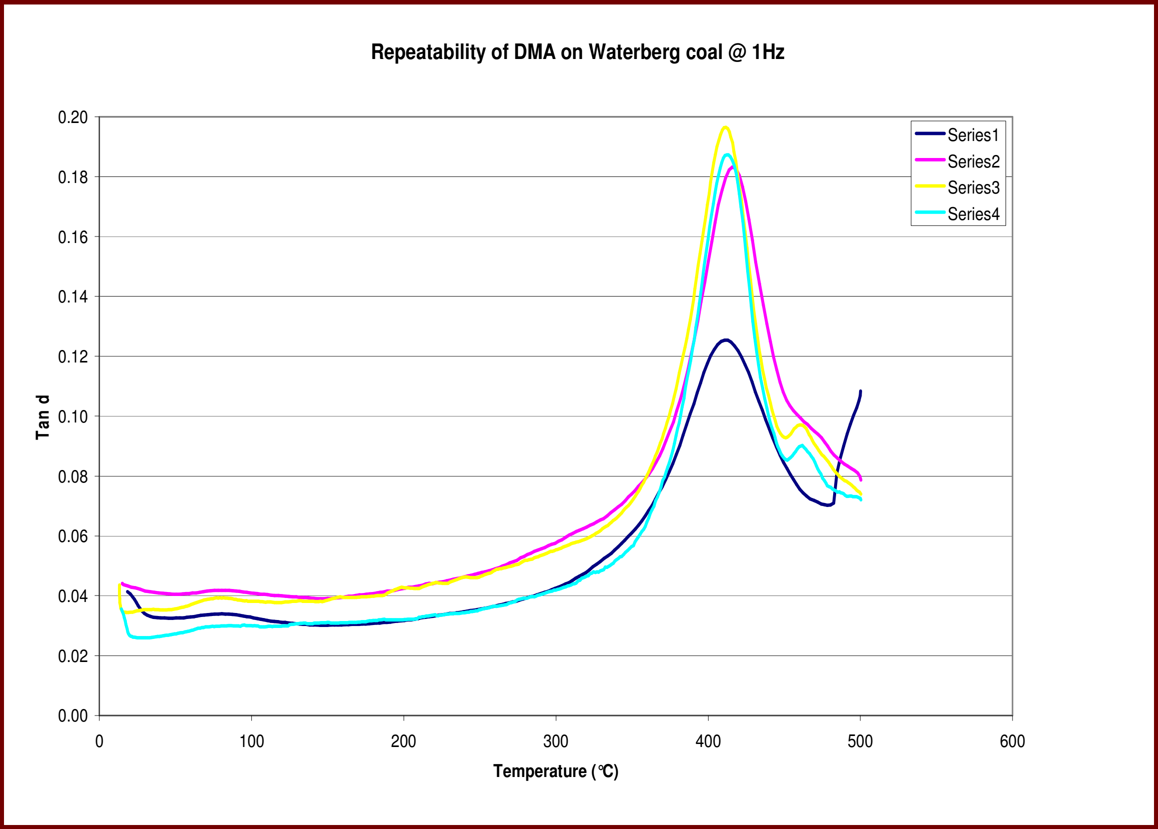
# The loss modulus, E”

- E” is a measure of the energy lost to friction and internal motions in the material.
- In the baseball analogy, it is what the ball does not recover—why it doesn’t bounce all the way back.
- $E'' = (\sigma/\varepsilon) \sin \delta$

# The all-important tan δ

- E"/E' = sin δ / cos δ = tan δ
- tan δ is the damping. It indicates how efficiently the material loses energy to molecular rearrangements and internal friction.
- tan δ is one of the most fundamental properties measured by DMA.
- One of our interests was the variation of tan δ with temperature.

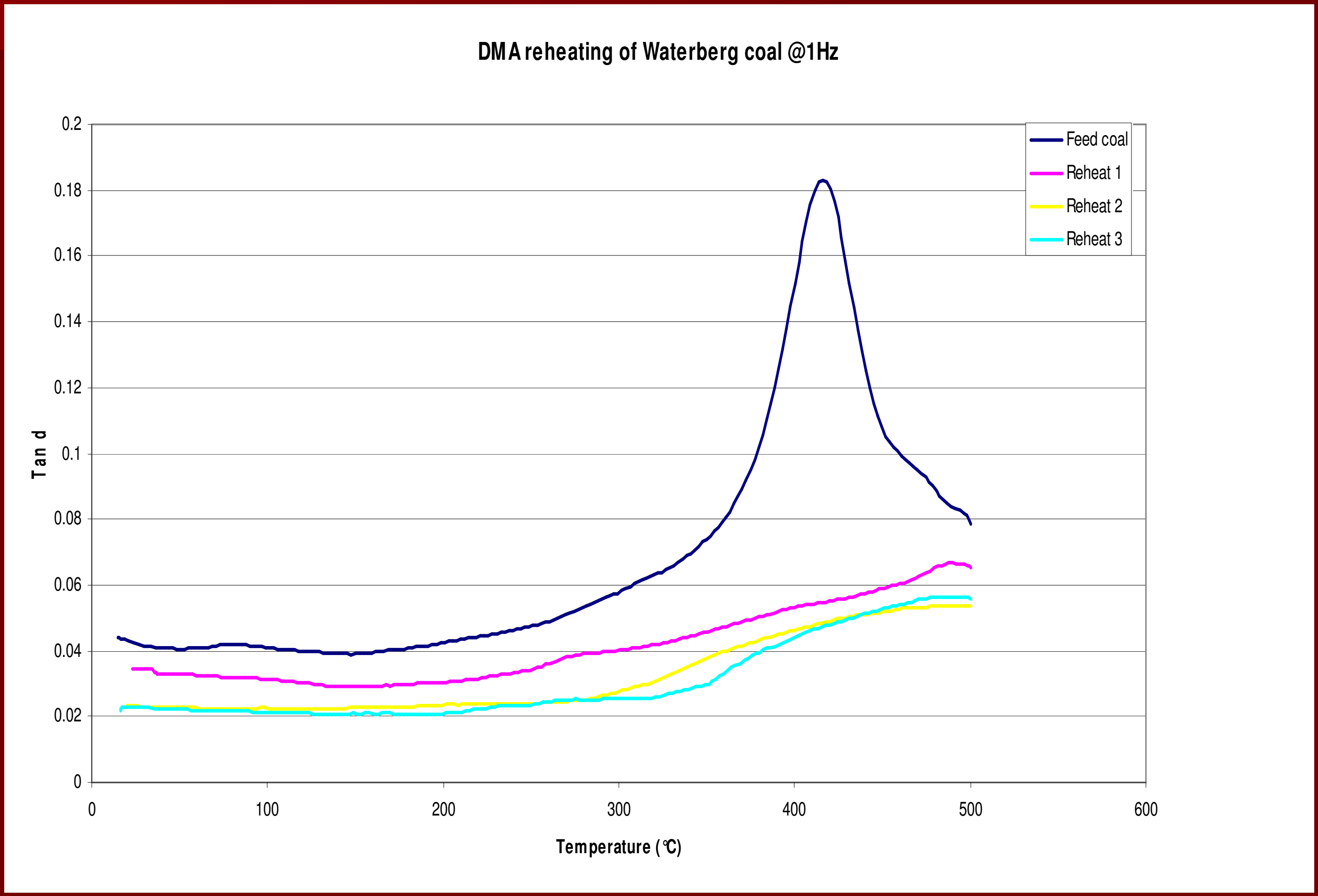
# Repeatability of tan δ vs. T for different samples of the same coal



# Effect of temperature on tan δ

- As temperature increases, tan δ increases. This means that E” is increasing relative to E’.
- More of the energy that is being applied to the sample is going into internal motions (structural rearrangements?) of the material.
- The maximum in tan δ vs. T suggests that a point is reached at which the structure has rearranged and internal motions become less important.
- This is reminiscent of, but not identical to, Gieseler fluidity for bituminous coals.

# Repeatability of tan δ vs. T for multiple runs on the same sample



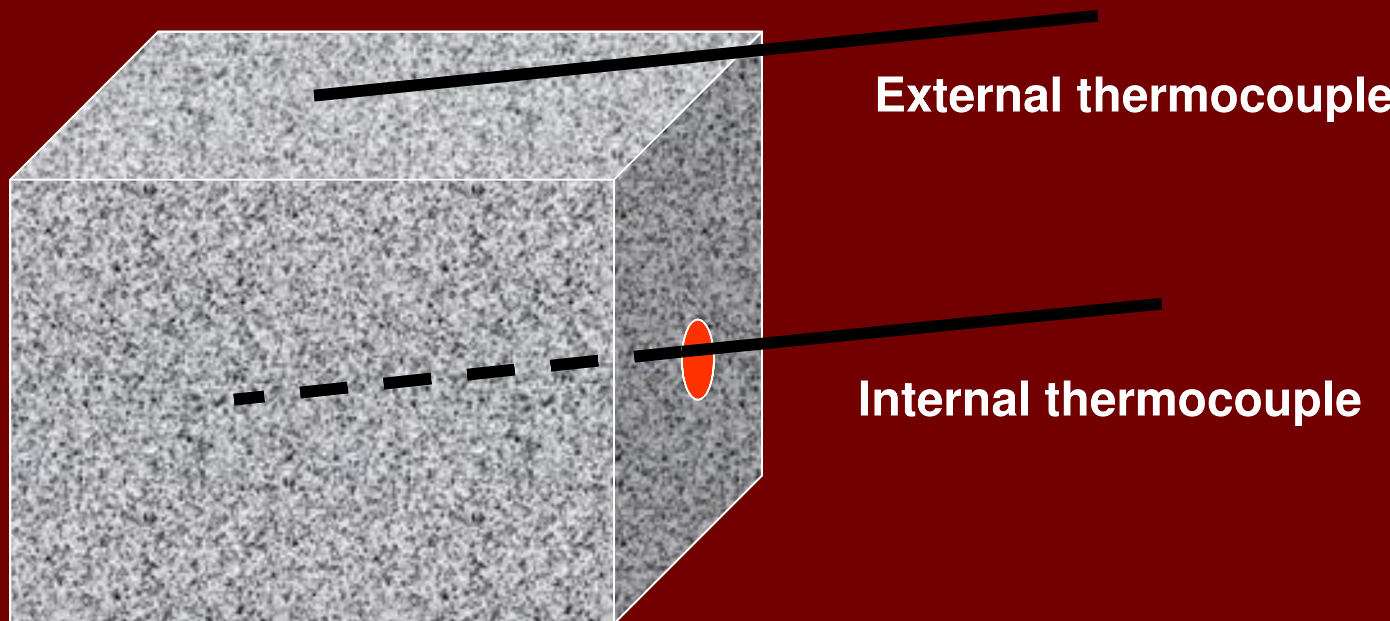
# Effect of repeat runs on tan δ vs. T

- Making successive tan δ vs. T measurements on the same sample shows that temperature + oscillating stress creates an irreversible change in the material.
- After the second (certainly third) run, the sample no longer rearranges as it did the first time. Runs 2, 3…. are basically identical.
- This appears to be very similar to John Larsen's work on solvent swelling of coals.

# Experimental protocol for assessing thermal conductivity

1. Prepare block of the coal sample, with thin hole drilled to the center.
2. Attach one thermocouple to external surface, insert second thermocouple to center of the block.
3. Insert this assemblage into oven preheated to the desired test temperature.

# Schematic of simple thermal conductivity experiment



# Anticipated results from thermal conductivity testing

- The external thermocouple output will rise very rapidly to the set temperature of the oven, and hold there for duration of the test.
- The internal thermocouple output will rise more slowly, because heat must be conducted through the coal block. Eventually it will also reach the set point of the oven.
- The “lag” between internal and external thermocouples is governed by the thermal conductivity of the coal.

# A trip down the wrong alley…

- In some tests done in an outside laboratory, the temperature indicated by the internal thermocouple went *higher* than that of the external thermocouple.
- **???????????????**
- To account for this, we hypothesized a spontaneous exothermic reaction occurring in the interior of the coal block.
- But, is such a reaction possible, and how can we test for it?

# Why could there be a spontaneous exothermic reaction inside a coal particle?

1. Most coals contain particles of pyrite. Pyrite, or its decomposition product pyrrhotite, can be a catalyst for coal reactions.
2. Hydrogen in coal can be shuttled around during coal reactions (e.g., the “net hydrogen” concept). Some coals can be good hydrogen donors.

# Experimental protocol to test for internal exothermic reaction

1. Salvage coal blocks showing the unusual internal heat. Embed in epoxy and cross-section.
2. Using FT/IR/Raman microscope, examine the block from outside surface inward, to detect region(s) of structural change and what such changes may have been.
3. Also examine by optical microscopy.

# Holmes on Theories

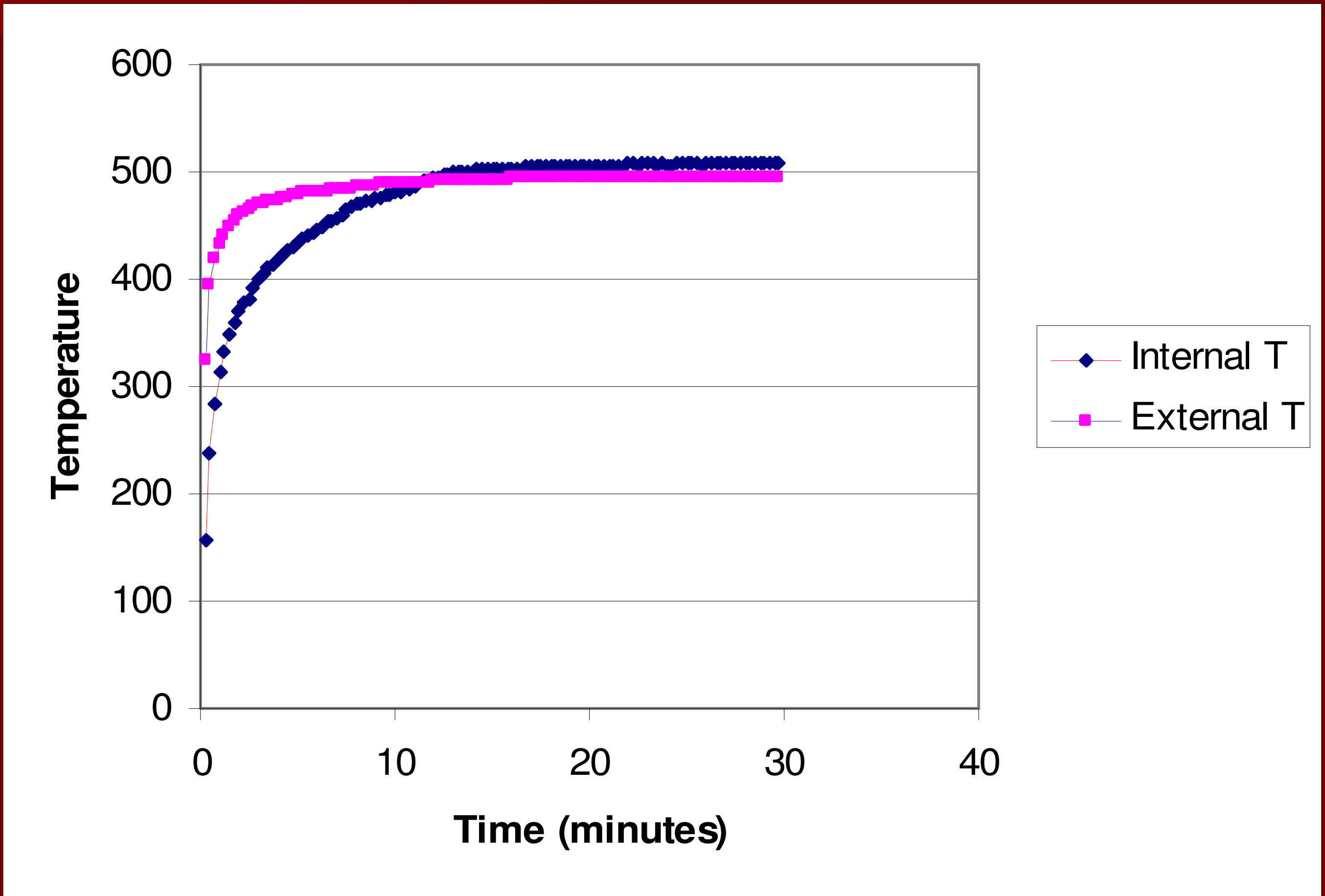
- It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts. *
- One forms provisional theories and waits for time or fuller knowledge to explode them. A bad habit…but human nature is weak.§

— *Sherlock Holmes*

*A Scandal in Bohemia

§ The Adventure of the Sussex Vampire

# The raw data for a hypothesized internal exothermic reaction



# Meaning of the internal temp. being higher than external temp.

- These data *are not* the signature of an internal exothermic reaction.
- They *are* the signature of people who don't know how to calibrate thermocouples.

# A beautiful hypothesis meets an ugly fact

# Experimental protocol to test for internal exothermic reaction

1. Salvage coal blocks showing the unusual internal heat. Embed in epoxy and cross-section.
2. Using FT/IR/Raman microscope, examine the block from outside surface inward, to detect region(s) of structural change and what such changes may have been.
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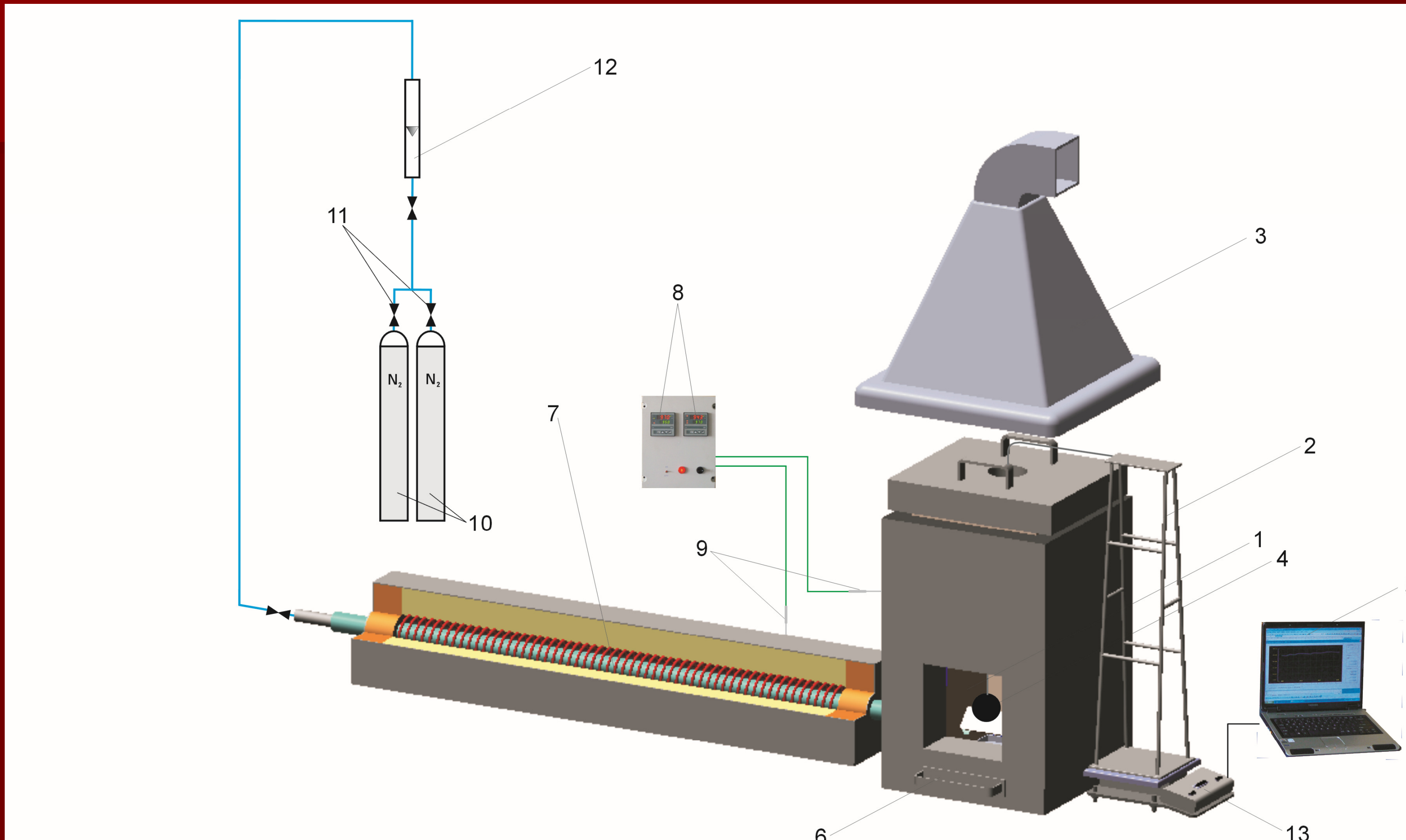
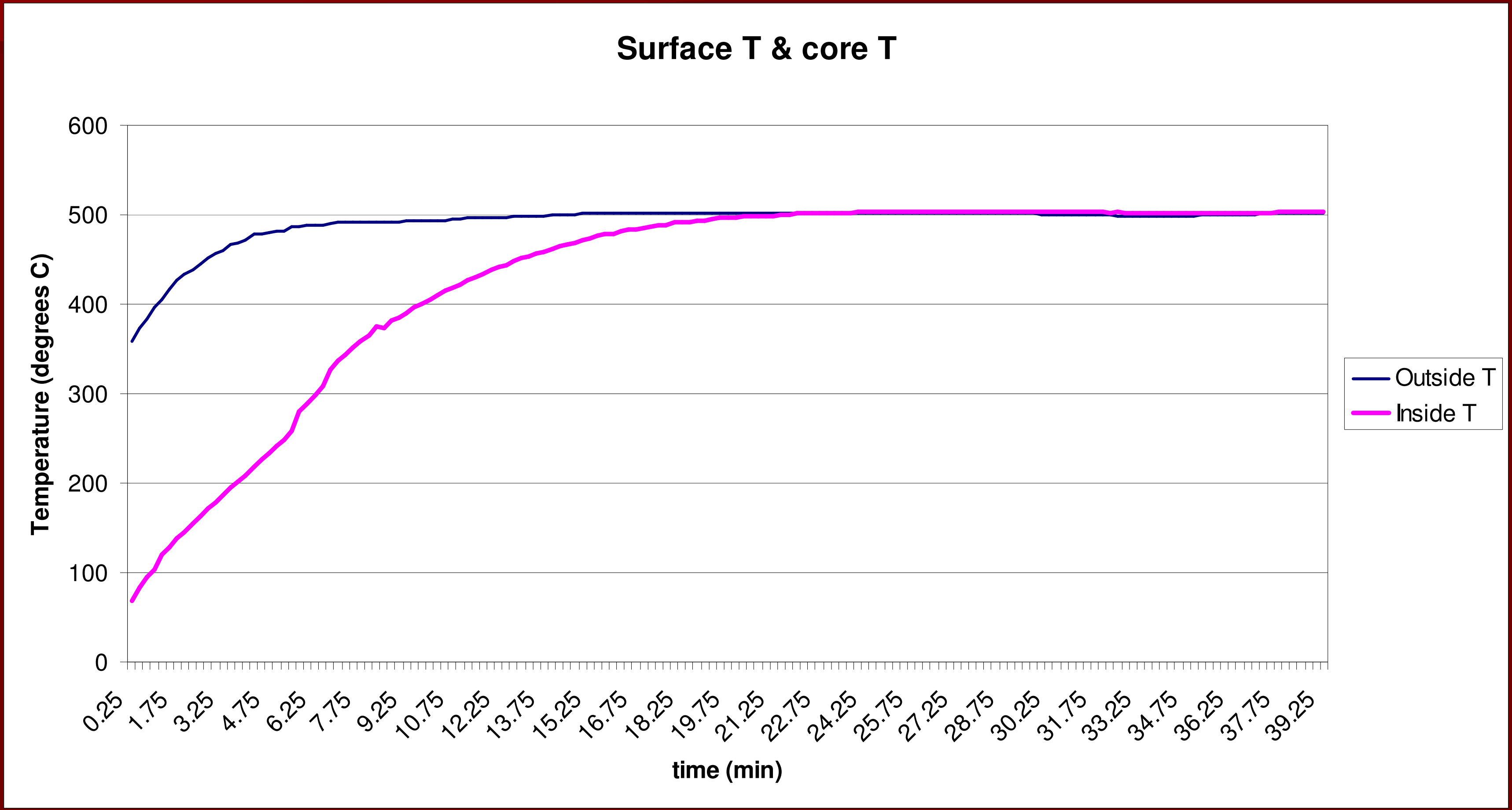
# Schematic of overall test apparatus

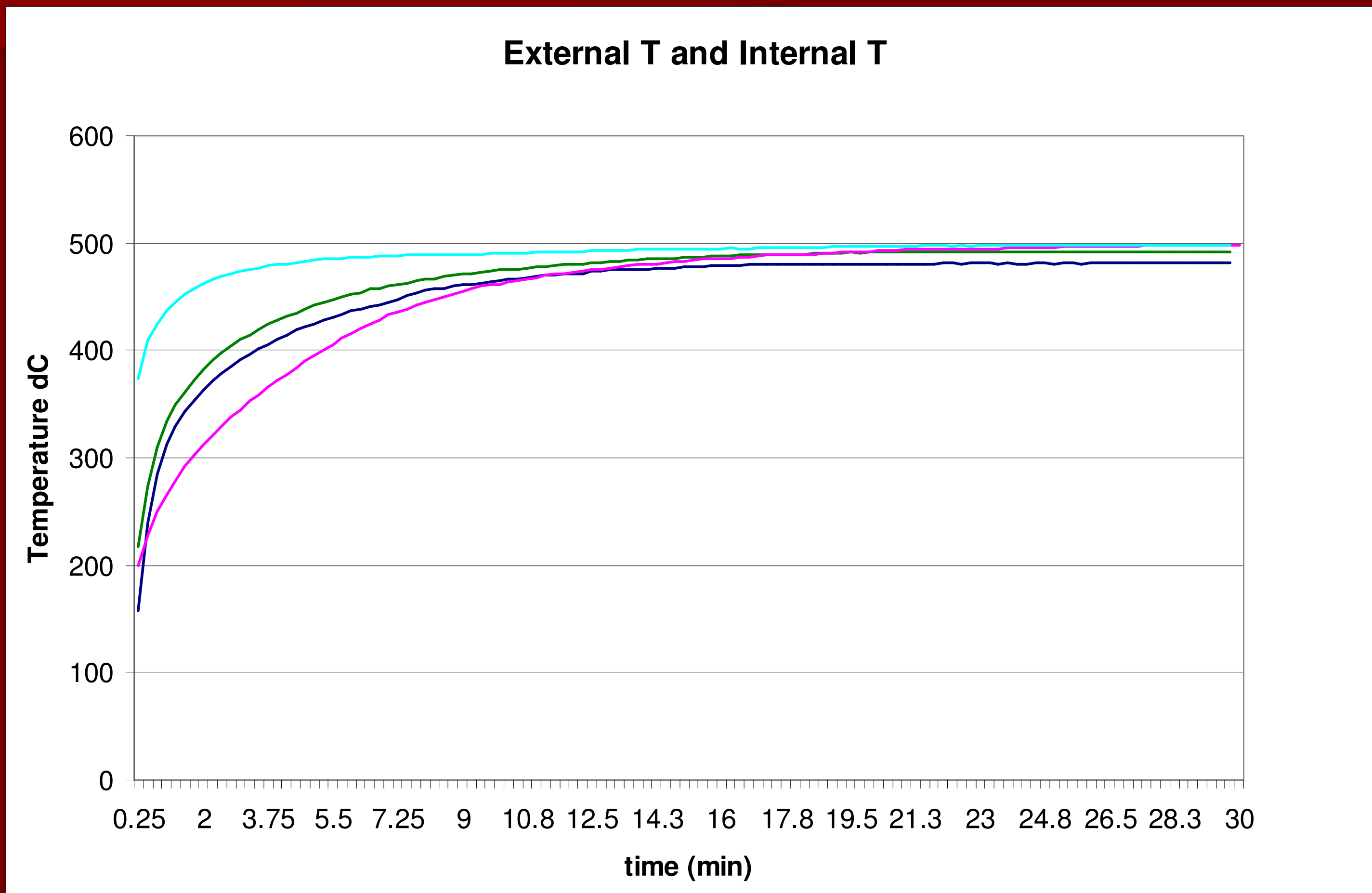



1 – reaction chamber, 2 – aluminium construction, 3 – exhaust gas, 4 – coal particle, 5 – computer, 6 – moving drawer, 7 – preheater, 8 – thermoregulator, 9 – K-type thermocouple, 10 – gas cylinder, 11 – pressure regulator, 12 – rotameter, 13 – laboratory balance

# Our work shows expected lag between interior and exterior T



# Repeatability of measurements for multiple runs on the same sample



# Effect of repeat runs on thermal conductivity of the same sample

- Successive thermal conductivity measurements on the same sample show an irreversible change after the first run.
- With the second and following runs, sample shows a higher thermal conductivity than in the first run. Runs 2, 3… are basically identical.
- This appears to be very similar to solvent swelling and to DMA.

# Mechanisms of heat conduction in solids

- Heat is transferred through solids by two "carriers": migration of free electrons and lattice vibrations.
- In quantum wave/particle duality, lattice vibrations can be considered as particles called phonons.
- Thus the thermal conductivity k is given as

$$k = k_e + k_{ph}$$

# Aspects of thermal conductivity in nonmetallic solids

- In nonmetallic solids, $k_{ph}$ dominates.
- $k_{ph}$ increases as the frequency of interactions between atoms and the lattice decreases, or as the phonon mean free path increases.
- Well-ordered materials usually have higher thermal conductivity than disordered materials.

See, e.g., Incropera et al., *Fundamentals of Heat and Mass Transfer*, Wiley, 2007.

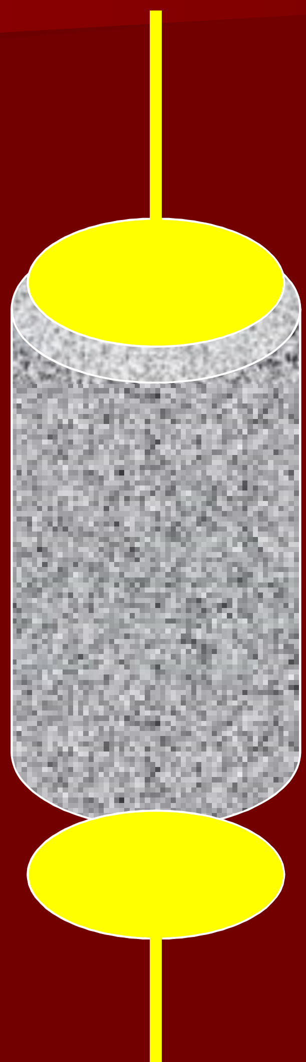
# Inferences from thermal conductivity testing

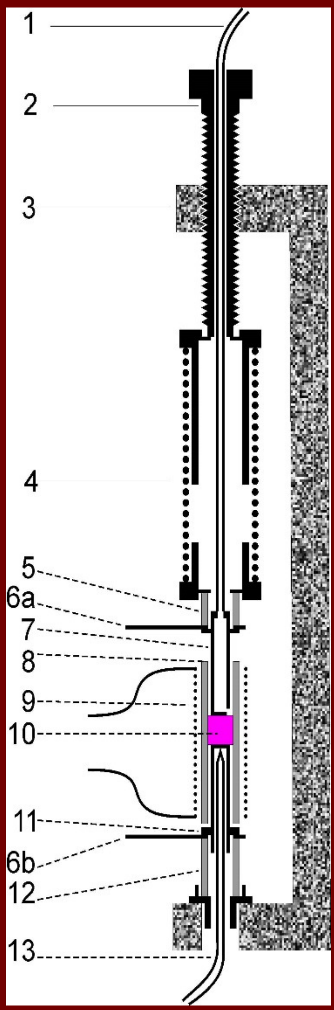
- An irreversible change occurs in the thermal conductivity as a result of one heating cycle.
- The increased thermal conductivity suggests that the structure has become more ordered (i.e., increased $k_{ph}$).
- Is there also an effect on $k_e$?

# Experimental protocol for assessing electrical resistance

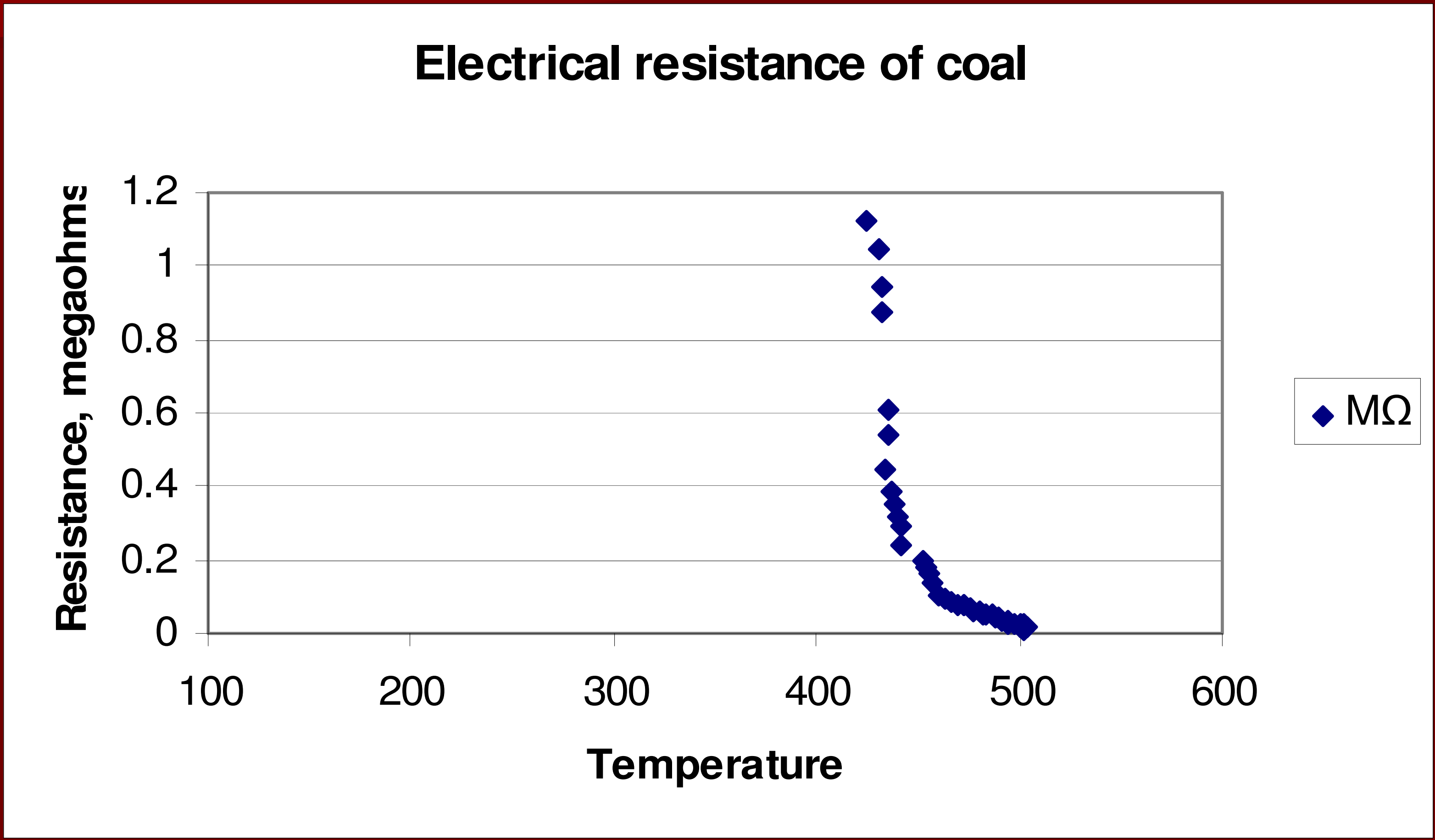
1. Prepare specimen of coal, and attach electrical connections to each end.
2. Connect multimeter; place the test specimen inside an oven.
3. Measure resistance as a function of temperature as the specimen is heated and cooled.

# Schematic of simple electrical resistance experiment

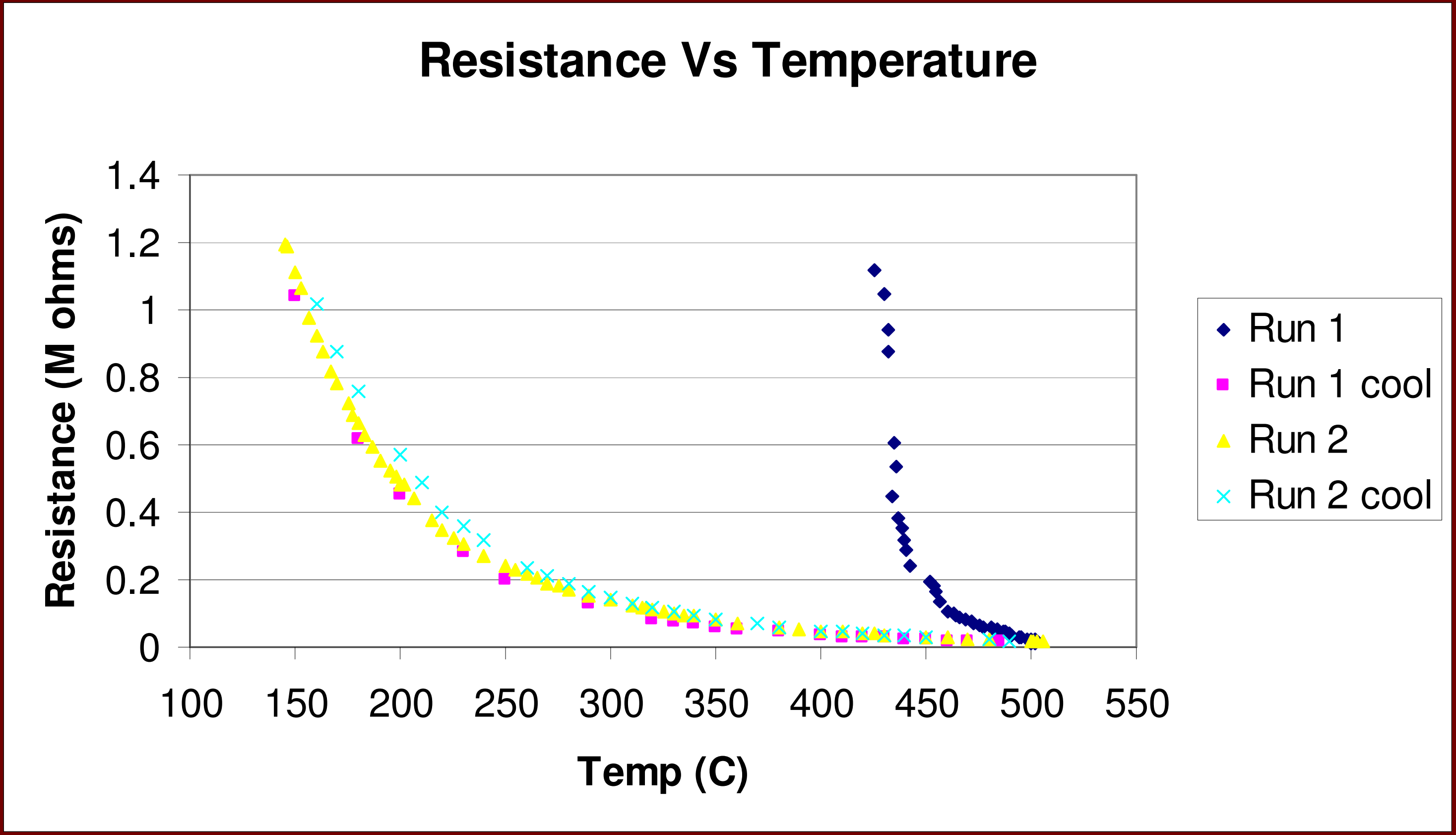




# Electrical resistance vs. temperature



# Repeatability of resistance for multiple runs on same sample



# Effect of repeat runs on electrical resistance of the same sample

- Successive electrical resistance measurements on the same sample show an irreversible change after the first run.
- With the second and following runs, sample shows a lower electrical resistance than in the first run. Runs 2, 3… are basically identical.
- This appears to be very similar to solvent swelling, to DMA, and to thermal conductivity.

# Mechanisms of electrical conduction in solids

- Electrical conduction is due to the movement of electrons. Conductors have a large density of free charges; insulators have most charges bound to atoms.
- A decrease of resistivity with increasing temperature (typical of semiconductors) means that increased thermal energy has increased the number of free charges available to carry current.

See, e.g., Urone, *College Physics*, Brooks/Cole, 2001.

# Inferences from electrical resistance testing

- An irreversible change occurs in the electrical resistance as a result of one heating cycle.
- The much lower electrical resistance suggests that the structure has changed to increase the population of free charge carriers and/or the mean free path of electrons.

# Putting it all together

- As T increases to ≈400°C, increasingly higher proportion of thermal energy goes into internal motion of the structure.
- Above ≈400°C, less of the applied thermal energy is "lost" in internal motions. This change is irreversible.
- Heating to ≈500°C causes irreversible increase in thermal conductivity, via $k_{ph}$ and/or $k_e$.
- Resistance is "off the charts" (literally!) to ≈425° C, then drops rapidly with further temp. increase.
- This heating causes irreversible reduction in resistance, indicating a structural change that created higher free electron density and/or greater electron mean free path.

# Immediate challenges…

- Using the temperature data to solve heat conduction equations for k (eventually $k_e$ and $k_{ph}$?).
- Converting measured resistances to resistivity ($\rho$), which is the intrinsic property of a material.
- Assessing the structural changes: high-temperature XRD, Pugmire's "Q-factor" by NMR, Raman, adding a GC "sniffer" to the ovens.
- Incorporating effects of structural anisotropy.

# … and speculations

- Coals catalyze electron-transfer reactions, particularly for a mis-match between numbers of electrons given up by reductant and accepted by oxidizer.* This could be related to electrical resistivity.
- Reflectance involves interaction of electromagnetic field of light with electrons at the solid surface. Is there a relation among vitrinite reflectance, electrical resistivity, and chemical reactivity?

*See Medina et al., *Fuel* **2005**, *84*, 1.

# Some potential applications…

- Using resistivity to determine the temperature to which a piece of coal has been exposed.
  - A paleo-thermometer in coal geochemistry
  - Understanding temperature distributions in coal conversion equipment
- Elucidating the nature of coal as a solid material, e.g. the true glass transition temperature.

# …and about diamonds

- Diamonds ($sp^3$ carbon) have very high thermal conductivity ($k_{ph}$) *and* very high resistivity.
- Can we sort out $k_e$, $k_{ph}$, and $\rho$ to assess the regions of ordered $sp^3$ and $sp^2$ (graphitic) carbon in a coal?

Acknowledgements

- Bafana Hlatshwayo and Gerda de Jager, who did all the work.
- John Larsen, Gerhard Lachmann and Christien Strydom, for collaboration.
- A large synthetic fuel company in the southern hemisphere, for support.

# Coming in 2010 to a bookstore near you…

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