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Arrhenius rate integrals in finite-element thermal solutions

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Arrhenius rate integrals can play an important role in thermal codes for biomedical applications. We have included support in **TDiff** and **HeatWave**. The purpose is find spatial regions where significant chemical changes have occurred in applications like RF tumor ablation. The changes induced in tissues by heating are not a simple function of the maximum temperature. Biological damage depends on both temperature and the time over which heating is applied. The reaction rate for any endothermic chemical reaction can be approximated by the Arrhenius expression:

$$\frac{dn}{dt} = -A \exp\left(-\frac{\Delta E}{RT}\right) n. \tag{1}$$

In the equation, n is the number of entities (molecules, living cells, ...) that have not yet reacted, R is the universal gas constant (8.315 J/mol-°K) and T is the temperature in °K. The two reaction parameters A and ΔE have units of s^{-1} and J/mol respectively. The exponential form reflects the fact that endothermic reactions involve a quantum tunneling process.

The equation has the solution:

$$\frac{n(t)}{n_0} = \exp\left[-\Omega(t)\right], \tag{2}$$

where

$$\Omega(t) = A \int_0^t dt' \exp\left[-\frac{\Delta E}{RT(t')}\right]. \tag{3}$$

In biomedical applications the quantity Ω is often called the *Arrhenius damage integral*. A value $\Omega = 1$ indicates that about 63% of the cells have been modified by the reaction.

During dynamic thermal solutions, TDiff and HeatWave determine the damage integral in all elements for which reaction-rate parameters have been defined. The postprocessors can plot spatial variations of Ω and can also determine surfaces of fixed Ω. One problem in implementing the capability is finding and interpreting values of A and ΔE. The first and second columns of the table of Fig. 1 list some values for mammalian tissue reported in the literature. Note that values of A vary by more than 200 orders of magnitude, and values of ΔE by about a factor of 40. We have developed alternate forms of the reaction parameters for the thermal programs that have two advantages:

- They have values that are in a reasonable range (≤ 1000).
- They have easily-understood physical meanings.

We can rewrite the equation for the Arrhenius damage integral in the form

$$\Omega(t) = \int dt' \exp\left(\Lambda\left[1 - \frac{T_c}{T(t')}\right]\right). \tag{4}$$

The two new parameters are related to the original ones by

$$\Lambda = \ln(A), \tag{5}$$

Tissue	A (1/s)	ΔE (J/mol)	Λ	Tc (degK)
Liver	7.39E39	2.58E5	91.8	337.7
Bulk skin	1.80E51	3.27E5	118.0	333.1
Tendon (rat tail)	6.66E79	5.21E5	183.8	341.1
Tendon (rabbit patella)	1.14E86	5.623E5	198.1	341.2
Cell death	2.98E80	5.06E5	185.3	328.7
Microvascular blood flow	1.98E106	6.67E5	244.8	327.7
Protein coagulation	7.39E37	2.58E5	87.2	355.4
Epidermis	3.10E98	6.27E5	226.8	328.1
Porcine epidermis	4.32E64	4.16E5	148.8	336.2
Chordae tendinae	1.30E53	3.57E5	122.3	351.0
Porcine epidermis	4.11E53	3.39E5	123.5	330.1
Rat skin collagen	1.61E45	3.06E5	104.1	353.5
Rabbit muscle	3.12E20	1.28E5	47.2	326.2
Human aorta	5.60E63	4.30E5	146.8	352.3
Kangaroo tendon	3.01E89	5.89E5	206.0	343.9
Lens capsule	3.85E137	8.60E5	316.8	326.5
RIT	6.66E79	5.21E5	183.8	340.9
RIT (acetic acid)	3.81E218	1.31E6	503.3	313.0
RIT	1.90E54	3.70E5	125.0	356.0
Porcine cornea	2.07E15	1.06E5	35.3	361.4
Joint capsule	4.00E5	3.40E4	12.9	317.0
Joint capsule	1.85E32	2.34E5	74.3	378.8

Figure 1: Arrhenius rate parameters for common mammalian tissues

and

$$T_c = \frac{\Delta E}{R\Lambda}. \tag{6}$$

These quantities are listed in columns 3 and 4 of Fig. 1. Note the values of the critical temperature T_c. Even though there are huge variations of A and ΔE between tissues, the critical temperature varies by less than 5%. Similarly, the temperature-range parameter Λ varies by only about a factor of 40.

We can understand the physical meanings of T_c and Λ by considering a system with fixed temperature T_0. In this case, the equation for Ω has the form:

$$\Omega = \Delta t \exp\left[\Lambda\left(1 - \frac{T_c}{T_0}\right)\right]. \tag{7}$$

The equation shows that when $T_0 = T_c$, the tissue reaches $\Omega = 1$ in a time interval $\Delta t = 1.0$ s. In other words, at the critical temperature 63% of the cells are deactivated within 1 second. In general, higher temperatures are required to alter tissues with higher values of T_c.

To understand the meaning of Λ, suppose that we limit attention to a relatively small range of temperature near T_c such that

$$T_0 = T_c - \Delta T \tag{8}$$

where $\Delta T \ll T_c$. In this case, we can solve for the time interval in the equation for Ω:

$$\Delta t \cong \Omega \exp\left(\frac{\Lambda\ \Delta T}{T_c}\right) \tag{9}$$

For given values of Ω and the fractional temperature difference $\Delta T/T_c$, the required heating time increases with higher values of Λ. As an illustration, consider calculation of the required heating time to reach $\Omega = 1$ for liver tissue at 50 °C ($T_0 = 323.15$ °K). Inserting parameters from the table into the above equation, we find that $\Delta t = 62.4$ s.