Reaction rates, explosions and dissipation

INTRODUCTION

The following question was posed by Dr (Luke) Burke:

If an exothermic (heat producing) reaction proceeds in isolation, the mixture will get hotter and hotter. Also, the rate of chemical reaction often increases with increasing temperature, so the reaction will proceed faster and faster and there is some danger of an explosion. In an effort to prevent this, the reaction could be cooled by placing the reaction vessel in contact with some ice. The question is, would the ice be sufficient to keep the temperature of the reacting material under control?

Objective

In this Lab you will simulate an exothermic reaction in contact with a block of ice which dissipates the heat.

The main question to be answered is, what happens to the temperature of the mixture after it has been reacting for a long time? Does the temperature; (i) continue to increase? (ii) increase at first and then level off? (iii) decrease to the temperature of the ice?

THEORY

The change in temperature T with time t for an exothermic first-order reaction coupled to a dissipative heat bath is

$$\mathbf{\frac{dT}{dt} = K_o e^{-\frac{E_A}{RT}} - D_o(T - T_o)} \tag{1}$$

Here

- D_o is the rate of dissipation of heat by the ice,
- T_o is the temperature of the ice,
- $K_o e^{-\frac{E_A}{RT}}$ is the reaction rate which is an increasing function of temperature.

The maximum possible rate, which occurs at $T = \infty$, is K_o, so the reactant cannot explode. In the approximation used here the rate is independent of the concentration of the reactant. This is not a very realistic approximation, since we know that the rate varies with concentration as,

$$\frac{d[\text{reactant}]}{dt} = -k[\text{reactant}]^\alpha$$

But when $t \simeq 0$ the concentration of the reactant is approximately constant,

$$[\text{reactant}(t)] \simeq [\text{reactant}(t = 0)]$$

and the reaction rate can be written as,

$$\frac{d[\text{reactant}]}{dt} \simeq K_o$$

where

$$K_o = -k[\text{reactant}(t = 0)]$$

So Eq. (1) is a reasonable short-time approximation, *ie* $t \simeq 0$.

Equilibrium Temperature T vs Dissipation Rate D

At equilibrium

$$\mathbf{\frac{dT}{dt} = 0}$$

and we can solve for the equilibrium temperature T_{eq} as a function of the dissipation rate D_o. At some dissipation rates there are two equilibrium temperatures, while at other dissipation rates there are none.

PROCEDURE AND LAB REPORT

1. Construct the function $f(D,T) = dT/dt$ using the folowing Maple syntax:

$$\mathbf{f} := (\mathrm{D},\ \mathbf{T}) \rightarrow \mathbf{e}^{(-\frac{1}{\mathrm{T}})} - \mathbf{T}\,\mathrm{D}$$

2. **Plot the reaction rate dT/dt :** using **smartplot3d**, for the range $T = -0.1, \ldots, 10$, $D = 0.1, \ldots, 0.6$ and $dT/dt = -0.5, \ldots, 0.5$.

3. **Plot T_{eq} :** using the following Maple syntax:
   > **with(plots);implicitplot(f(D,T)=0,D=0..0.6,T=0..10);**

4. Once you have the T_{eq} plot, **print it out**. Remember that the plot gives you regions where the rate $dT/dt = 0$.

5. **Mark regions on the plot where the temperature is increasing, $dT/dt > 0$, and decreasing, $dT/dt < 0$.** To figure out whether the temperature is increasing or decreasing, use,

   eval$(f(D,T), [D = 1.0, T = 3.0]);$

6. Once you have the increasing and decreasing temperature regions marked, comment on whether, for each value of D, the temperature will increase to ∞, increase to some finite value, or decrease to T_o (temperature of the ice).