Auto ignition Temperatures of binary Mixtures at Elevated Pressures

Many chemical processes are run at elevated pressures and temperatures. If explosive mixtures are present, hot surfaces may be an effective ignition source. Because at the moment there is no general pressure dependence existing, the knowledge of the substance specific pressure dependence of the auto ignition temperature is important to define type and amount of system compatible explosion measures. Therefore investigations on auto ignition temperatures at elevated pressures up to 15 bar on binary mixtures (11 binary mixtures of flammable substances, 4 aqueous mixtures with at least 3 different composition) and the respective pure substances have been carried out to derive estimation methods.

For the measurements an apparatus and a procedure developed by PTB was used. The ignition criterion is either an steep temperature raise of at least 20 K or a steep pressure raise of at least 5 %. Taking into account data of pure substances published earlier by PTB the following results can be given:

The concentrations at which the auto ignition temperatures are found are high (molar amount between 25% and 40%) The respective concentrations are near to the upper explosion limit inside the explosion range at that temperature and pressure.
Pressure dependence for pure substances and binary mixtures:

The auto ignition temperatures decrease with increasing pressure whereas normally the largest decrease occurs between the auto ignition temperature at ambient pressure and the data at 2 bar. For pressures larger than 5 bar the decay mostly is very low. The pressure dependence of the auto ignition temperature follows a SEMENOFF correlation. This allows to interpolate and extrapolate (to a certain amount) if 2 (better 3) auto ignition temperatures at elevated pressures are known.

Dependence on the mixture composition:
The auto ignition temperatures of the mixtures are in no case lower than the auto ignition temperatures of the respective pure substances at the same pressure.
There is no linear dependence of the auto ignition temperatures on the composition. In contrary at elevated pressures the auto ignition temperature increases remarkably only at concentrations of about 85% of that substance having the higher auto ignition temperature. The reason is the weak concentration dependence of the auto ignition temperature at elevated pressures. Therefore at a certain pressure the respective auto ignition temperature of the binary mixture can be estimated using the concentration dependence of the auto ignition temperature of the pure component having the lower auto ignition temperature.

This is also possible for aqueous mixtures. If the concentration dependence is unknown the auto ignition temperature of the pure component having the lower auto ignition temperature can be used up to molar amounts of the component having the higher auto ignition temperature of 85%.

It is possible to estimate the auto ignition temperatures for further elevated pressures if the dependence of the auto ignition temperature on the composition of a binary mixture is known at one elevated pressure as well as the pressure dependence of the auto ignition temperature of the both pure substances. For such estimations the use of the auto ignition temperature determined at ambient pressure is however not suitable . Orienting measurements showed that the auto ignition temperatures in a closed vessel at 1 bar can be remarkably lower then the auto ignition temperature according to DIN 51794 in the open vessel.