Adiabatic Compression or Flow Friction Heat

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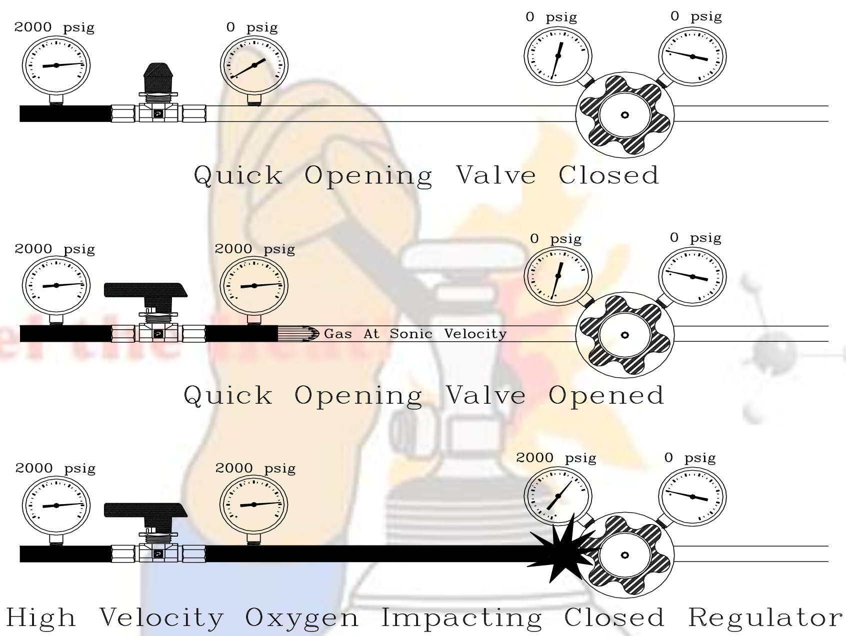
Reaction of certain unstable gases or reactive gas mixtures can be initiated because of adiabatic compression heat or flow friction heat from the system.

Adiabatic compression

Adiabatic compression occurs every time a cylinder valve of a high pressure gas cylinder is opened and gas flows into the low pressure downstream piping, rapidly pressurizing that system. Adiabatic compression occurs because the pressurization of the gas is so rapid that there is no time for the heat of compression to dissipate into the surrounding piping and valves. This rapid compression of the gas generates elevated gas temperatures that can ignite a flammable material or dissociate a gas like NF_3.



Heat of compression vary based on gas. For example

Compression Ratio, P_2/P_1	Air, °C (K = 1.40)	Isobutane, °C (K = 1.11)
5	199	77
10	302	101
20	429	120
23.5	462	134
50	639	166
100	838	197

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\kappa - 1)/\kappa}$$

Where K = ratio of heat capacities

Germane

100 psig	282°F (139°C)
200 psig	352°F (178°C)
300 psig	397°F (203°C)
400 psig	430°F (221°C)
500 psig	458°F (237°C)
569 psig	615°F (324°C)
1000 psig	1303°F (706°C)

Of significance is the influence of pressure. At 0 psig the autoignition temperature of germane in air was 145-150°C. Pressurizing it to 500 psig dropped it to less than 20°C.[1,2]

At least one incident occurred due to this. A cylinder containing germane was immersed in LIN it somehow sucked in and liquefied air. When the valve was opened on a gas manifold the heat of compression ignited the mixture and the reaction caused the cylinder to propel itself upward. The cylinder imbedded itself in the hood above.

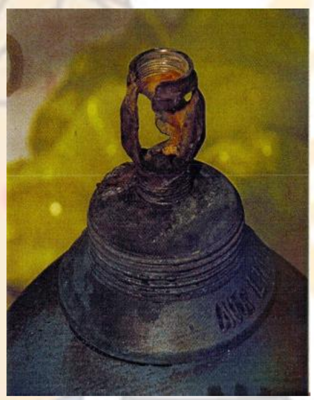
As NF_3 is an oxidizer, consideration must be given to the following issues when designing systems to handle NF_3:

materials of construction and compatibility of lubricants and sealing compounds
minimization of the effects of adiabatic compression
gas velocities
initial cleanliness and passivation
valve types
filter materials
operating procedures
maintenance procedures
separation of NF3 from flammable gases (see also 6.9)
heat dissipation
compression

Flow friction

That is what happened with this 12 cylinder bundle of NF_3. One cylinder was not filled. The operator opened the cylinder valves and the high pressure NF_3 came rushing into the empty cylinder. Flow friction across the Kel-F valve seat caused it to ignite. This triggered the decomposition reaction of the NF_3 forming F_2.

Operators working with F_2 must wear new latex or nitrile gloves to prevent contamination of the gasket when they handle it. It also protects them from any HF in the old gasket.



Flow friction or adiabatic compression in cylinder bundle

Improperly cleaned or maintained regulators have exploded due to this reaction. For example

Oxygen fires have been caused because of surface contaminants in the system interior such as machine oil or metal particle impact. Metals such as aluminum or titanium should not be used in high pressure oxygen service due to their reactivity. Aluminum can ignite at pressures as low as 25 psig (Alloy 6061) while 304 stainless steel will not ignite until 725 psig. Aluminum and carbon steel are the worse metals for oxygen service. They will burn at a pressure as low as 15-25 psig. As a result, brass is the preferred metal for a pressure regulator.

Medical E aluminum regulator recall due to numerous fires (1994-2000)

Flow friction ignition due to reuse of plastic crush gasket

Oxygen enrichment is at 23.5% or higher. Flammable materials will burn faster or ignite quicker.

Systems require slow opening valves.

Adiabatic compression heat occurs every the time a gas system is pressurized. The key is the compatibility of the materials. In general the metal systems such as brass or stainless steel will not react.

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References:

1. "Hazardous Properties of Germane Mixtures", HRC Report 5879A to Matheson Gas Products, Hazards Research Inc., Oct 28, 1985
2. "Hazardous Properties of Germane Mixtures", HRC Report 5879B to Matheson Gas Products, Hazards Research Inc., April 10, 1986
3. CGA G-14, Code of Practice for Nitrogen Trifluoride (EIGA Doc. 92/03),2nd Edition, 2010