SAFETY in the Operation of Laboratory Reactors and Pressure Vessels

The User's Responsibility

All Parr reactors and pressure vessels are designed and manufactured with great care to ensure safe operation when used within their prescribed temperature and pressure limits. But the basic responsibility for safety when using this equipment rests entirely with the user, who must:

1. Select a reactor or pressure vessel which has the capacity, pressure rating, corrosion resistance, and design features that are suitable for its intended use. Parr engineers will be glad to discuss available equipment and material options with prospective users, but the final responsibility for selecting a reactor or pressure vessel that will perform to the user's satisfaction in any particular reaction or test must rest with the user – not with Parr.

   Parr reactors and pressure vessels are offered in several different styles, each designed for convenient use in daily operation within certain temperature and pressure limits, using gaskets, O-rings, closures and other elements carefully selected for safe operation within the limits specified for that design. But in order to preserve the validity of these designs, all temperature and pressure limits must be observed, and no attempt should be made to increase these limits by making alterations or by substituting components which are not recommended by the manufacturer.

2. Install and operate the equipment in a suitable barricade, if required. Use appropriate safety accessories and operate in full compliance with local safety codes and rules.

   All standard Parr pressure vessels are provided with either a suitable relief device or a means to attach one (typically in the form of a plugged opening). When a pressure vessel is delivered without a pressure venting device, it is the customer's responsibility to provide pressure relief in order to protect the operator and the equipment from destructive high pressures. If you need more information or need help in selecting a proper relief device, please contact Parr Instrument Company.

3. Establish training procedures to ensure that any person handling the equipment knows how to use it properly.

4. Maintain the equipment in good condition and establish procedures for periodic testing to be sure that the vessel remains structurally sound.

Consider the Chemistry

Since safety in bench scale pressure reactions is so closely related to the chemistry involved in the process, there are several basic questions that the operator must always consider before starting to use pressure equipment:

Is the reaction exothermic? What by-products will be produced and what will be their behavior? What maximum temperature and pressure limits will be observed? Under what circumstances (temperature, pressure and catalyzing agents) might the reaction run out of control? By considering these and any other related safety questions before starting a pressure operation, the user should be able to anticipate any violent chemical behavior and take steps to prevent it.

Reactions involving highly reactive compounds such acetylene, butadiene, dioxane, ethylene oxide, oxygen, and all strong oxidizing agents must be handled cautiously. Close attention must also be given to any reactions that might release sudden surges of heat or pressure and to any by-products or end-products suspected to have explosive or detonating properties. It is always advisable to run preliminary experiments using small volumes of reactants when starting work with new or unfamiliar materials. The amounts can be increased later after it has been shown that the reaction proceeds smoothly with no indication of erratic or explosive behavior.

I Didn't Know it Was Loaded!!

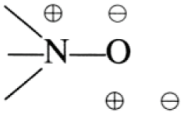
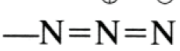
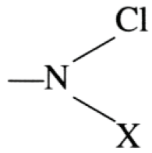
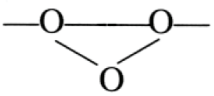
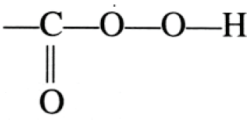
H.K. Livingston, Guest Editor, Department of Chemistry, Wayne State Iniversity, Detroit, Michigan.

Many a chemist has expressed amazement *after* an explosion, at which time he learned that his explosion could have been predicted from a knowledge of the chemistry of materials he used in the experiment, "I didn't know it would explode" is as weak an apology for a chemist as "I didn't know it was loaded" is for a rifleman. An integral part of one's laboratory technique is preparing for what might happen.

A definitive list of all the chemicals that could explode would be convenient, but chemistry deals with too many materials to make such a list practical. Therefore we resort to the same methods that we use to handle the complexity of chemicals when we are considering other chemical properties. We generalize and classify our information, always remembering that there are no hard and fast rules in chemistry and we must retain our over-all understanding of chemistry to interpret each specific situation.

Explosions in the chemistry laboratory result from reactions that liberate heat or volumes of gas or both. By working on a small scale, as we always should with unknown reactions, we minimize the chance that liberation of heat alone will lead to an explosion. We can then concentrate our attention on those reactions that can lead to a sudden increase in volume. This increase can be so sudden that the pressure cannot be relieved and an explosion, or even a detonation (CHEMISTRY, October 1964, IBC), can result. Here are 18 atomic groupings that, in the mind of the experienced chemist, are associated with the possibility of explosion (Table I). If you are running an experiment with any of these, even on a small scale, your experiment may be "loaded." Not only should you not point it at any one, but you should work behind an adequate safety shield. That is, in the opinion of someone who has had experience with these particular chemicals, the shield should be considered adequate for the experiment in question.

TABLE I. Atomic Groupings That Characterize Explosive Compounds

Name	Structure
Acetylide	—C≡C—Metal
Amine oxide	
Azide	
Chlorate	$—ClO_3$
Diazo	—N=N—
Diazonium	$(—N{\equiv}N)^{\oplus}X^{\ominus}$
Fulminate	—O=N=C
N-Haloamine	
Hydroperoxide	—O—O—H
Hypohalite	—O—X
Nitrate	$—O—NO_2$
Nitrite	–O—NO
Nitro	$—NO_2$
Nitroso	—NO
Ozonide	
Peracid	
Perchlorate	$—ClO_4$
Peroxide	—O—O—

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Barricades and Ventilation

The room in which a pressure reactor is to be operated must be well ventilated. This is particularly important when working with flammable or toxic materials. The reactors should be located close to a laboratory hood or exhaust fan so that any released gases can be discharged safely. There should be no open flames in adjacent areas.

Most Parr reactors are usually operated in an open laboratory without additional barricades or protective screens, but the operator must realize that additional protection may be necessary if there is any possibility that the reaction might run out of control. In case of an accident or unexpected overpressure, the safety rupture disc should burst to relieve the vessel before it is damaged by excess pressure. Therefore, provisions must be made to handle the noise and any potential fume hazards created by this release. Extension piping attached to the safety rupture disc fitting and leading to an appropriate discharge area offers the best protection against this possibility. Ear protection is also recommended, since the loud report produced by a bursting rupture disc may damage the hearing of anyone standing near the reactor.

It must also be remembered that certain explosive reactions proceed with such speed that the shock wave created by the explosion may damage the vessel before the rupture disc can dump the excess pressure. The best protection against this hazard is to operate the reactor behind a suitable barricade or in a pressure test cubicle or cell.

If a barricade is required, it should be built of concrete, brick or steel in whatever thickness or form is considered necessary to protect the operator from flying fragments if the apparatus should explode. Glass shields, either plain or reinforced with wire mesh, are not recommended. The requirements for barricades differ so widely that each should be designed and built in order to protect against the potential hazards inherent in each installation. This subject is well covered in numerous textbooks and literature references on laboratory safety and high pressure technology, some of which are named in the “REFERENCES” section.

Loading Limits

One of the most subtle and frequently overlooked hazards that can arise in pressure vessel operation is that produced by overfilling the vessel. A vessel must never be filled to more than two-thirds of its available free space, and in some cases the charge must be reduced even further for safe operation. Dangerous pressures can develop suddenly when a liquid is heated in a closed vessel if the available free space is not sufficient to accommodate the expansion of the liquid. This is particularly true of water and water solutions which may increase to as much as three times their initial volume when heated from room temperature to the critical point at 374 °C. If the free space in the vessel is not sufficient to accommodate this expansion, destructive pressures will develop very suddenly and unexpectedly.

Although this problem can arise when heating any fluid, it is particularly dangerous when working with water, as shown by the data tabulated below. At temperatures up to 200 °C the increase in volume is small. But as temperature is raised higher, the fluid expands to fill 150% of its original space at 321 °C, and to more than three times its original space at the 374 °C critical point.

To prevent damage from this type of expansion, the amount of water placed in any sealed pressure vessel should not exceed the volume determined from the following formula for Maximum Allowable Water Loading (MAWL):

$$\text{MAWL} = \frac{(0.9)\,(\text{Vessel Volume})}{(\text{Volume Multiplier at Max. Temp.})}$$

Example:
What is the maximum volume of a water slurry which can be treated safely to 300 °C in a 1000 mL vessel?

Substituting in the above formula:

$$\text{MAWL} = \frac{(0.9)\,(1000)}{1.4} = 643 \text{ mL}$$

From the above it is clear that the vessel should not be charged with more than 643mL of slurry at room temperature. Good practice would dictate that the charge should be held somewhat below this theoretical maximum.

LIQUID VOLUMES AND VAPOR PRESSURES FOR WATER IN A CLOSED VESSEL AT ELEVATED TEMPERATURES					
Temperature ° F	°C	Specific Volume of the Liquid, cu.ft./lb.	Vapor Pressure, psig	Volume Multiplier, $Sp.V_T/Sp.V_{77°F}$	% Volume Increase
77	25	.01607	—	1.00	0
212	100	.01672	0	1.04	4
392	200	.01853	211	1.15	15
482	250	.0201	562	1.25	25
540	282	.0215	948	1.34	34
572	300	.0225	1230	1.40	40
610	321	.0241	1650	1.50	50
660	349	.0278	2350	1.73	73
685	363	.0315	2780	1.96	96
700	371	.0369	3070	2.30	130
702	372	.0385	3120	2.40	140
704	373	.0410	3160	2.55	155
705	374	.0503	3190	3.13	213
(Critical Point)					

Data from Keenan & Keyes, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York

Design Pressure and Temperature Limits

The maximum design pressure and temperature limits for any pressure vessel will depend upon the design of the vessel and the strength of the materials used in its construction. Since all materials lose strength at elevated temperatures maximum design pressures are always associated with a design temperature limit. Each Parr vessel is clearly stamped with its maximum design pressure and temperature limits. No vessels should ever be used above these indicated limits.

In some cases the "standard" design maximum pressure limits can be increased if stronger materials are used or if the maximum operating temperature is reduced. In all cases any changes must be evaluated by the Parr Engineering Department before the vessel is manufactured, tested and certified.

Operating Pressure and Temperature Limits

In all cases the maximum operating pressure will be somewhat less than the maximum design pressure. In some cases the maximum operating temperature may also be lower than the design temperature.

The principle reason for reducing operating pressures and or temperatures below the design pressure is the installation of components on the vessel which do not carry the same pressure rating as the vessel itself. Operators may select valves with special characteristics which are rated for lower pressures and/ or temperatures. Users may prefer lower range gages which provide better resolution for their own operating ranges. Substituting different gasket materials can significantly reduce operating temperatures.

The ASME Pressure Vessel Code limits the maximum burst pressure of the required rupture disc to the maximum design pressure of the vessel The European Community Pressure Equipment Directive allows these discs to be up to 110% of the design pressure. Our recommendation is to limit maximum operating pressures to not more than 90% of the design burst pressure of the installed rupture disc. For most users this will limit the maximum operating pressure to 90% of the design pressure.

The Parr Engineering Department is always available to answer any questions regarding either design or operating pressure and/ or temperature limits.

Maintenance and Training

Users must realize that it is their responsibility to keep the reactor in good condition and to use it only within the prescribed temperature and pressure limits. Users must be constantly aware of the serious consequences that can result from such things as: opening the wrong valve, mixing combustible vapors with air or oxidizing gases, adding reactants too fast or failing to observe and prevent a sudden increase in temperature or pressure. Supervisors should make frequent checks to be sure that all safety rules are being observed. In the absence of a supervised safety program the user must take time to become completely familiar with their equipment and to consider any hazards inherent in the reactions they intend to perform.

Materials of Construction

Although Parr reactors and pressure vessels made of Type 316 stainless steel are suitable for most of the applications in which this equipment is used, there are many operations which require pressure vessels made of other metals or alloys. The list of construction materials available for use in Parr pressure equipment is shown in the table below. Each of these alloys has its own physical strength and temperature characteristics, as well as its own unique resistance to certain corrosive agents.

Parr now uses alloy designation numbers instead of trade names to identify the various corrosion resistant alloys available for use in Parr equipment. Many of the high nickel varieties were originally patented and sold under trade names, such as Monel$_1$, Inconel$_1$, Incoloy$_1$, Carpenter Alloy$_2$, Hastelloy$_3$, and others. Most of the original patents have expired and these alloys are now available from more than one supplier, as well as from the owner of the original trade name. With materials of almost identical composition and equal corrosion resistance now available from more than one supplier, Parr will select and offer the most widely used alloy in each of the basic corrosion resistance categories without being limited to particular trade names. The corrosion resistance and suitability of these alloys for specific applications are summarized in the listings below.

Any abridged listing of corrosion resistance can be potentially misleading since it cannot possibly deal with all of the effects of concentration, temperature, pressure and the presence of additional ions, all of which have a significant effect upon the ability of a particular metal alloy to withstand corrosion. In addition, the vulnerability of any material to stress corrosion cracking, intergranular corrosion and pitting must also be considered when judging the suitability of a material for a particular application. The listings which follow are intended to serve only as a starting point for any study of the comparative corrosion resistance and physical properties of the construction materials available for use in Parr pressure equipment. Additional details can be obtained from individual alloy manufacturers and from other sources.

Nominal Chemical Composition Of Pressure Vessel Materials

Major Elements — Percent

Material	Fe	Ni	Cr	Mo	Mn	Other
T316 Stainless Steel	65	12	17	2.5	2.0	Si 1.0
Alloy 20Cb-3	35	34	20	2.5	2.0	Cu 3.5, Cb 1.0 max
Ally 400	1.2	66				Cu 31.5
Alloy 600	8	76	15.5			
Alloy B-2	2	66	1	28	1	Co 1.0
Alloy C-276	6.5	53	15.5	16	1	W 4.0, Co 2.5
Nickel 200		99				
Titanium Grade 2		Commercially pure titanium			Ti 99 min	
Titanium Grade 4		Commercially pure titanium			Ti 99 min	
Zirconium Grade 702		Zr + Hf 99.2 min Hf 4.5 max				
Zirconium Grade 705		Zr 95.5 min, Hf 4.5 max, Co 2.5				

1 MONEL, INCOLOY and INCONEL are Registered Trademarks of Special Metals.

2 CARPENTER 20Cb-3 is a Registered Trademark of Carpenter Technology Corporation.

3 HASTELLOY is a Registered Trademark of Haynes International, Inc.

Type 316 Stainless Steel is an excellent material for use with most organic systems. A few organic acids and organic halides can, under certain conditions, hydrolyze to acetic, formic and other organic acids that are routinely handled in T316SS.

T316SS is not normally the material of choice for inorganic acid systems. At ambient temperatures it does offer useful resistance to dilute sulfuric, sulfurous, phosphoric and nitric acids which readily attack T316SS at higher concentrations and temperatures. Halogen acids attack all forms of stainless steel rapidly, even at low temperatures and in dilute solutions.

T316SS offers excellent resistance to surface corrosion by caustics, but this is misleading. Caustics can cause stress corrosion cracking in stainless pressure vessels. This phenomenon begins to appear at temperatures just above 100 °C and has been the most common cause of corrosion failure in stainless laboratory vessels.

T316SS does offer good resistance to ammonia and to most ammonia compounds.

Halogen salts can cause severe pitting in all stainless steels. Chlorides can cause stress corrosion cracking, but many other salt solutions can be handled in stainless vessels, particularly neutral or alkaline salts.

At moderate temperatures and pressures, T316SS can be used with most commercial gases. In a scrupulously anhydrous system even hydrogen chloride, hydrogen fluoride and chlorine can be used in stainless steel.

Alloy 20 Cb-3 is an enriched grade of stainless steel, designed specifically for use with dilute (up to 30% by weight) sulfuric acid at elevated temperatures. It can also be used for nitric and phosphoric acid systems as well as for all systems for which T316SS is suitable.

Alloy 400 is comprised essentially of two-thirds nickel and one-third copper. For many applications it offers about the same corrosion resistance as nickel, but with higher maximum working pressures and temperatures and a lower cost because of its greatly improved machinability.

Alloy 400 is widely used for caustic solutions because it is not subject to stress corrosion cracking in most applications. Chloride salts do not cause stress corrosion cracking in Alloy 400. It is also an excellent material for fluorine, hydrogen fluoride and hydrofluoric acid systems. Alloy 400 offers some resistance to hydrochloric and sulfuric acids at modest temperatures and concentrations, but it is seldom the material of choice for these acids. As would be expected from its high copper content, Alloy 400 is rapidly attacked by nitric acid and ammonia systems.

Alloy 600 is a high nickel alloy offering excellent resistance to caustics and chlorides at high temperatures and high pressures when sulfur compounds are present. In caustic environments, Alloy 600 is unexcelled. It is often chosen for its high strength at elevated temperatures. Although it can be recommended for a broad range of corrosive conditions, its cost often limits its use to only those applications where its exceptional characteristics are required.

Alloy B-2 is an alloy rich in nickel and molybdenum which has been developed primarily for resistance to reducing acid environments, particularly hydrochloric, sulfuric and phosphoric. Its resistance to these acids in pure forms is unsurpassed, but the presence of ferric and other oxidizing ions in quantities as low as 50 ppm can dramatically degrade the resistance of this alloy.

Alloy C-276 is a nickel-chromium-molybdenum alloy having perhaps the broadest general corrosion resistance of all commonly used alloys. It was developed initially for use with wet chlorine, but it also offers excellent resistance to strong oxidizers such as cupric and ferric chlorides, and to a variety of chlorine compounds and chlorine contaminated materials. This alloy is used extensively to combat the high temperature and high pressure corrosive conditions encountered in drilling for sour petroleum deposits and in other oil field applications.

Alloy 200 is one of the designations of commercially pure nickel. It offers the ultimate in corrosion resistance to hot caustic environments, but its applications are severely restricted because of its poor machinability and resultant high fabrication costs.

Titanium is an excellent material for use with oxidizing agents such as nitric acid, aqua regia and other mixed acids. It also offers very good resistance to chloride ions. Reducing acids, such as sulfuric and hydrochloric, which have unacceptably high corrosion rates in pure titanium can have their corrosion rates reduced to acceptable levels if relatively small quantities of oxidizing ions, such as cupric, ferric, nickel or even nitric acid are present to act as corrosion inhibitors. This phenomenon leads to many successful applications for titanium in the hydrometallurgy field where acids, particularly sulfuric acid, are used to leach ores. In these operations the extracted ions act as corrosion inhibitors.

Prospective users must remember that titanium in the presence of oxygen at elevated temperature and pressures will burn vigorously. While there have been many successful applications in hydrometallurgy where oxygen and sulfuric acid are handled in titanium equipment, the danger of ignition is always present and must be protected against whenever titanium and oxygen are used together.

Commercially pure titanium is available in several grades. Grade 2 is the material most commonly used for industrial equipment since it can be fabricated by welding and is approved by the ASME Code for Unfired Pressure Vessels. Grade 4 which has slightly higher trace levels of iron and oxygen, has higher strength than Grade 2 but it is not suitable for welding and it is not covered by the ASME Code. Since Parr vessels are not welded, they usually are made of Grade 4 to obtain the higher working pressures than can be obtained with Grade 2. Grade 7 contains small amounts of palladium, and Grade 12 contains small amounts of nickel and molybdenum. These grades of Titanium offer enhanced resistance to certain environments and can be used for Parr reactors and pressure vessels if suitable billets can be obtained.

Zirconium offers excellent resistance to hydrochloric and sulfuric acids but, as with Hastelloy B-2, oxidizing ions such as ferric, cupric and fluorides must be avoided. Zirconium also offers good resistance to phosphoric and nitric acids and to alkaline solutions as well. Two different grades are available: Grade 702 containing hafnium is the standard commercial grade offering the best resistance to most corrosive agents. Grade 705 contains small amounts of both hafnium and columbium and has better strength than Grade 702 allowing higher working pressures when it is used in pressure vessel construction. The corrosion resistance of Grade 705 is not quite as good as Grade 702.

Carbon Steel is usually used for laboratory reactors only when it is desired to duplicate construction material used in plant equipment. Because it rusts easily, carbon steel vessels are not carried in stock and must be made to order, often resulting in costs higher than for stainless steel equipment despite the lower material cost for carbon steel.

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