could be fired repeatedly without entering the test chamber.

The only drawback to the use of a thermocouple for flame detection was that it required an arbitrary definition of the temperature rise produced by a flame. It was necessary to know whether the flame actually came in contact with the thermocouple. In most cases this was obvious. However, in a few cases intermediate temperature rises resulted from flames which traveled part way up the pipe and were then quenched. In these cases it was necessary to define arbitrarily the amount of temperature rise caused by a flame propagation. The effect of this arbitrariness on the flammable limits was small.

The distance of 2 feet between the igniter and the detector was also arbitrary. This distance had to be great enough so that the detector was not influenced by the ignition source. Two feet appeared to be sufficient. As a flame travels through a tube, a certain amount of heat is transferred from the flame front to the vessel walls. In small tubes this heat loss narrows the flammable limits. As a general rule the effect is negligible if the vessel diameter is 5 cm. or greater (*1*), a condition satisfied by the present 2-inch internal diameter chamber.

A limited number of runs indicated that increasing the pressure in the flame chamber from atmospheric to 15 p.s.i.g. caused a change in the flammable limit of about 1% in the air-rich direction. Because Andrussow hydrogen cyanide reactors normally operate under a pressure of about 1 atm. gage, all determinations were carried out at 15 p.s.i.g. in order to eliminate pressure effect as a variable.

Mixtures of flammable gases in the vicinity of their flammable limits have a certain statistical probability of propagating a flame. The curve of per cent flame propagation *vs.* composition roughly represented these statistical probabilities. This curve is an S-shaped curve which asymptotically approaches 100 and 0% flame propagation. Because the curve never reaches the line of 0% propagation, it is necessary to define arbitrarily the point at which the mixture is no longer considered flammable. This was done in these tests by extending the slope of the inflection of the S curve until it intersected the line of 0% flame propagation (Figure 1). In most cases the intersection was at a composition which has less than a 5% probability of propagating a flame.

As a check on the rotameter calibrations, several gas mixtures were sampled and chemically analyzed for per cent ammonia. In every case the analyzed composition fell within ±0.5% (absolute) of the calculated composition.

Extrapolation of the data to the Andrussow catalyst temperature of 1000° to 1100° C. is probably not justified. It has been found unnecessary to do so, however, because results from a test reactor indicate that gas mixtures lying on the 500° C. flammability line (by extrapolation) will not flash back from the Andrussow catalyst at flow rates as low as 0.5 linear foot per second.

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Hydrogen Cyanide Stability and Heat of Polymerization

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SOME TIME ago a steam-traced, heavily insulated 5-gallon container which was being used as a partial vaporizer for hydrogen cyanide exploded in one of the company laboratories. Because this company manufactures hydrogen cyanide and stores it in quantity, it was necessary to find out what caused the explosion, what could be done to prevent similar explosions, and whether hydrogen cyanide was likely to decompose with explosive violence under ordinary conditions of storage and use.

A literature survey revealed only three reports of studies of the stability of hydrogen cyanide under various conditions. Walker and Eldred (*3*) investigated the stability of hydrogen cyanide at several pressures and temperatures in steel bombs heated by a gas flame. They also tested ammonia, sodium hydroxide, and sodium cyanide as polymerization initiators and sulfuric acid and copper as inhibitors. Wohler and Roth (*4*) showed that hydrogen cyanide is a powerful explosive that can denonate completely on very strong initiation. Sporzinsky and Salter (*2*) studied the effects of various oxalates as inhibitors at 100° C.

This investigation covered the effects of temperature, sodium hydroxide, water, hydrogen cyanide polymer, and "weathered" hydrogen cyanide on the length of time that hydrogen cyanide can be held without violent polymerization; and the effect of the relative amount of hydrogen cyanide in a container on the incubation time. The heat of polymerization of hydrogen cyanide at 25° C. has also been determined.

EXPERIMENTAL

Stability Studies. These studies were carried out in the explosion bomb shown in Figure 1. The bomb was constructed of super pressure tubing, 5/8 inch in inside diameter and 1-7/8 inches in outside diameter. It was equipped with a 10,000 p.s.i. rupture disk, strain gage, and thermocouple. The strain gage was connected to a recorder and the thermocouple to a recorder controller. The bomb was heated by two Nichrome ribbon heaters wrapped around an insulated copper sleeve which slipped over the body of the bomb.

A 1/4 replicate, 2^5 factorial experiment was used to evaluate the effects of temperature, sodium hydroxide concentration, weathering, water content, and hydrogen cyanide polymer content on the stability of hydrogen cyanide. The conditions for each run and the results are given in Table I.

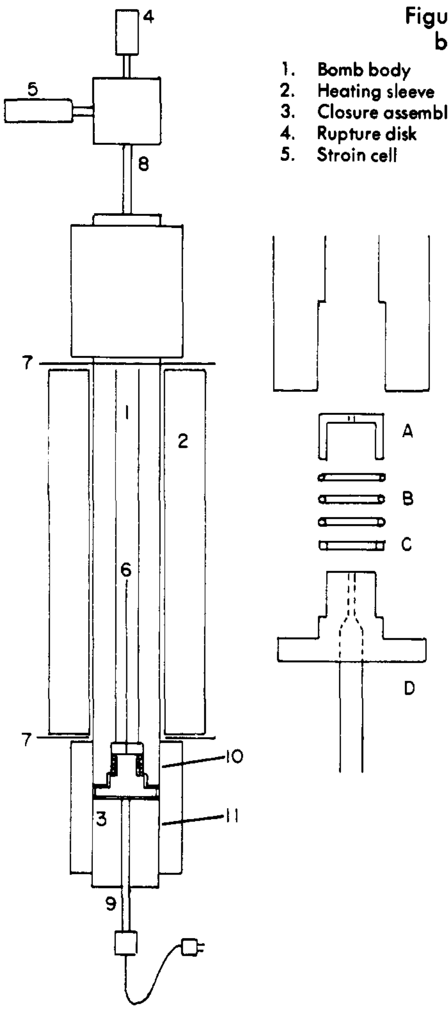

Figure 1. Diagram of explosion bomb and detail of closure

1. Bomb body
2. Heating sleeve
3. Closure assembly
4. Rupture disk
5. Strain cell
6. Thermocouple
7. 1/32-inch phenolic insulating disks
8. 3/8-inch super pressure tubing
9. 1/4-inch super pressure tubing
10. Pipe threads
11. Machine threads

A. Closure extractor
B. Teflon O rings
C. Steel seal ring
D. Super pressure tubing

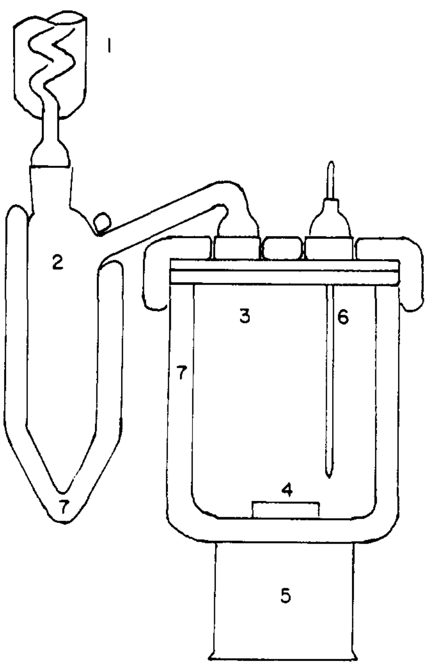

Figure 2. Diagram of heat of polymerization equipment

1. Spiral condenser, ice water-cooled
2. Receiver
3. 2-liter resin kettle
4. Stirrer bar
5. Magnetic stirrer
6. Thermometer
7. Insulation

Table I. Designed Experiment to Determine Effect of Several Variables on Stability of Hydrogen Cyanide

Run No.	Temp., °C.	NaOH, Mmole/G. HCN	Weathered HCN, %	Water Added, %	HCN Polymer Added, %	Incubation Time, Min.
1a	175	14×10^{-5}	10	7	1	1
2a	100	0	0	7	1	104
3a	175	0	0	0	1	6
4a	175	0	0	0	0	27
5a	100	14×10^{-5}	10	0	1	596
6a	175	14×10^{-5}	0	7	0	9
7a	100	0	10	7	0	2709[a]
8a	100	14×10^{-5}	0	0	0	1330[a]
9a	137.5	7×10^{-5}	5	3.5	0.5	23
10a	137.5	7×10^{-5}	5	3.5	0.5	23
1b	175	0.0204	10	7	1	−6
5b	100	0.0204	10	0	1	123
6b	175	0.0204	0	7	0	−3
8b	100	0.0204	0	0	0	304
9b	137.5	0.0102	5	3.5	0.5	5

[a] Reaction discontinued after these times.

INCUBATION TIME. The time elapsed between reaching the control temperature and the onset of violent reaction, as evidenced by a sudden rise in temperature, was used as a measure of the stability of hydrogen cyanide. Weathered hydrogen cyanide was obtained by allowing plant hydrogen cyanide (1.5% water, 0.1% sulfur dioxide as sulfuric acid) to evaporate to one fourth its volume.

Hydrogen cyanide was always present in the amount of 50 cc. In the runs with weathered hydrogen cyanide, 45 cc. of plant hydrogen cyanide and 5 cc. of weathered hydrogen cyanide were measured. The other ingredients were added in excess of this amount. During the runs made to evaluate the effect of the amount of hydrogen cyanide in the bomb, the strain cell and rupture disk were removed. Different amounts of hydrogen cyanide were charged to the bomb and heated to 175° C. and the incubation time was recorded.

Heat of Polymerization of Hydrogen Cyanide. The reaction was carried out in a 2-liter resin kettle equipped with a special receiver, ice water-cooled reflux condenser, and thermometer. The kettle top and receiver were insulated with glass wool inside glass fiber cloth. A heating mantle was used to insulate the body of the kettle (Figure 2). A magnetic stirrer was used to stir the reacting mixture. A blank of 500 cc. of hydrogen cyanide was stirred for 6 hours to determine the heat of stirring. Duplicate determinations of the heat of polymerization were made by adding triethylamine catalyst to 500 cc. of hydrogen cyanide in the kettle. After about 6 hours the reaction was stopped by adding acid. The hydrogen cyanide collected in the receiver was weighed. The unpolymerized hydrogen cyanide was evaporated from the kettle and the residue was weighed. The amount of polymer produced was calculated by subtracting the weight of the water in the hydrogen cyanide, the weight of the catalyst, and the weight of acid from the weight of the residue after evaporation.

The heat of polymerization was calculated from the specific heat of hydrogen cyanide, the amount of it distilled overhead, the amount of polymer produced, and the heat of stirring. The complete data are given in Table II.

DISCUSSION

Stability Studies. DESIGNED EXPERIMENT. The 1/4 replicate fractorial design (*1*) was chosen on the assumption that the effects of the indepent variables would be linear and that no interaction would occur. This system can be described by an equation of the form

$$Y = A_0 + A_1x_1 + A_2x_2 + A_3x_3 + A_4x_4 + A_5x_5$$

The x_i's are in factorial units and have the following significance

$$x_i = \frac{\text{desired level} - \text{av. exptl. level}}{\text{av. exptl. level} - \text{min. exptl. level}}$$

and

Table II. Heat of Polymerization of Hydrogen Cyanide

Run[a, b]	Time, Hr.	HCN Distilled, G.	Polymer Produced, G.	Temp., ° C.		ΔT	H, Stirring, Cal.	Catalyst	Wt. Catalyst, G.	Acid		$\Delta H_{\text{Pol.}}$, Cal./G.
				Initial	Final					Type	Wt., g.	
Blank	5-2/3	2.2	...	18	24.5	6.5	1921	...	...	...	...	...
1	6	16.1	8.2	27	27	6	1920	Triethylamine	7	Acetic	4.7	364
2	6	33	15.7	22	25	3	1920	...	10.5	Oxalic	13.5	389

[a] 500 cc. (350 grams) HCN used in each determination.

[b] Water content 1.5%.

x_1 = temperature in factorial units
x_2 = sodium hydroxide concentration in factorial units
x_3 = weathered hydrogen cyanide concentration in factorial units
x_4 = water concentration in factorial units
x_5 = polymer concentration in factorial units

The minimum temperature of 100° C. was chosen because incubation times below 100° C. would be prohibitively long. During a trial run with only hydrogen cyanide in the bomb, the controller was set at 180° C. The temperature rose to the critical 183.5° C. and a violent reaction occurred immediately. For this reason 175° C. was chosen as the maximum temperature, because adequate control was unlikely any closer to the critical temperature.

The original plans included recording pressure as well as temperature. This proved impossible because of a weakness in the design of the bomb. The 3/8-inch super pressure tubing used to connect the reaction chamber of the bomb to the strain cell plugged with polymer as soon as a reaction began, effectively isolating the pressure recording system. The pressure recorder did function nicely during the heating and incubation periods. The time-pressure charts were useful in several runs in ascertaining the exact beginning of a reaction, because the recorder showed a slight rise in pressure before the small tube plugged. There was no practical way to overcome this difficulty.

The results of runs 1a through 10a were used to develop an equation describing the effects of the variables on the stability of hydrogen cyanide. All constants were evaluated for significance. The coefficients of x_2 and x_3, describing the effects of sodium hydroxide and weathering, were found to be nonsignificant and eliminated. The equation is

$$\log t = 1.7814 - 1.0955x_1 - 0.2588x_4 - 0.491x_5 \quad \sigma = 0.341 \qquad (1)$$

A check showed that the amount of sodium hydroxide used reduced the inhibitor content from 0.0143 to 0.0142 mmole per gram. This change is so small that these runs can be considered to have been made without any added sodium hydroxide.

Runs 1, 5, 6, and 8 were repeated with the sodium hydroxide concentration at 0.0204 mmole per gram. Run 9, an average level run, was repeated using 0.0102 mmole per gram. Its effect was very pronounced. In the two runs at 175° C. reaction occurred before the control temperature was reached. In the runs at 100° C. and the average level run at 137.5° C., reaction occurred in about one fifth the time required in the first set of runs.

All 15 runs were then used to evaluate the stability of hydrogen cyanide. Because the first set of data correlated in terms of the log of the incubation time, it was necessary to convert the negative times of runs 1b and 6b to positive values. Run 1b was assigned a value of 1 minute and 7 minutes were added to the observed incubation times of runs made at 175° C. No changes were made in the times at 135.5° and 100° C.

When the coefficients of the five variables were calculated, those corresponding to the effects of water and weathering were found nonsignificant. The equation is

$$\log t = 1.4770 - 0.9128x_1 - 0.3289x_2 - 0.2923x_5 \quad \sigma = 0.505 \qquad (2)$$

The statistical nonsignificance of these coefficients is not due necessarily to any actual lack of effect, but more likely to masking of the effect of the particular variable by more powerful contributions of other variables in the system. The effect of water was significant in the absence of sodium hydroxide. When sufficient sodium hydroxide is added to the system, the effects of temperature, base concentration, and polymer concentration combine to mask the contribution of water to the shortening of the incubation time.

Figures 3 and 4 are comparisons of the observed and calculated values of log t using Equations 1 and 2, respectively. The agreement between the observed results and the incubation times calculated by Equation 1 is fairly good. The agreement of Equation 2 is poor. The disagreement is due mainly to lack of fit in assuming a linear model for the system.

Another comparison of the two equations is the incubation time predicted at 25° C. for pure hydrogen cyanide.

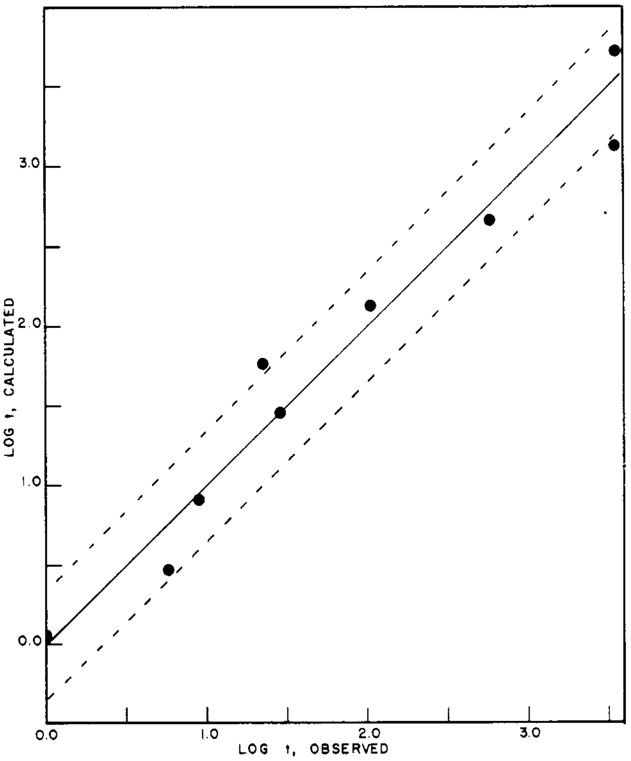

Figure 3. Comparison of $\log_{10} t$, calculated with $\log_{10} t$, experimental for Equation 1

----σ limits

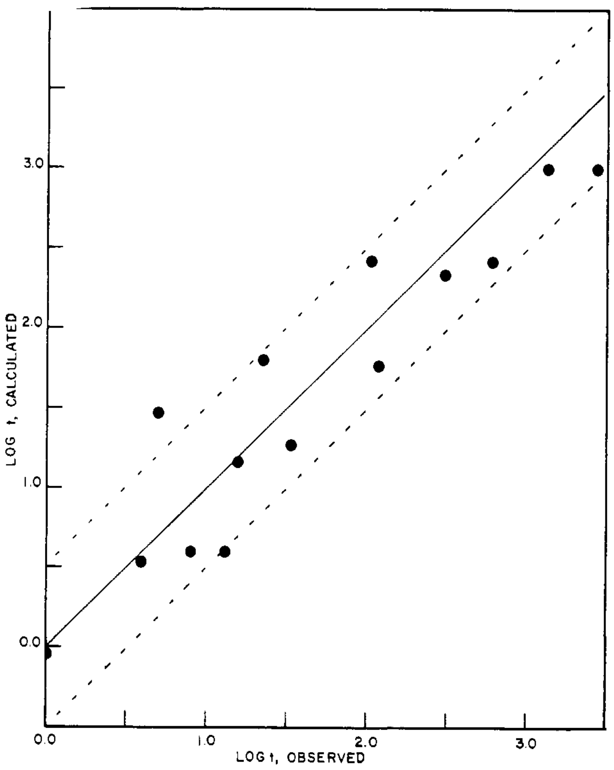

Figure 4. Comparison of $\log_{10} t$, calculated with $\log_{10} t$, experimental for Equation 2

-----σ limits

Equation 1 predicts 10,733 hours (15 months); Equation 2, about 1170 hours (1.6 months). The value predicted by Equation 2 is far short of the time that hydrogen cyanide is known to be stable.

If it is desired to predict the stability of hydrogen cyanide under reasonably mild conditions, Equation 1 will probably give a good value. In the case of hazardous conditions, Equation 2 is probably better, not because of any greater accuracy, but because its inaccuracy is heavily weighed toward predicting short incubation times.

VOLUME EFFECT. Incubation time is an inverse function of the amount of hydrogen cyanide in the bomb. Figure 5 is a plot of incubation time *vs.* the ratio of the volume of liquid hydrogen cyanide charged to the volume of the container. Linear plots are obtained when the data are converted to incubation time *vs.* the reciprocal of the ratio used above as the abcissa, or to log incubation time and log of the ratio of the volume of hydrogen cyanide to the volume of the container.

This effect has been studied in a particular bomb; therefore, the general quantitative applicability of these results is doubtful. However, they show the way in which the amount of hydrogen cyanide in a container influences the incubation time.

Heat of Polymerization. This determination was undertaken to provide an idea of the order of magnitude of the heat of polymerization of hydrogen cyanide, this information being needed for sizing relief valves. Because the precision and elegance of the usual calorimetric techniques were not desired, the simple method used in this study worked out. The theory behind the method is that in a well-insulated container the heat loss from the system is negligible and the entire heat of reaction will be used to vaporize unreacted hydrogen cyanide. The heat of polymerization can then be calculated from the heat of vaporization, the change in temperature of the system, and the heat input of the stirrer

$$\Delta H_{\text{Pol.}}/\text{g.} = \Delta H_{\text{vap.}} + C_p \Delta T - \Delta H_{\text{stirring}}$$

The results are in reasonably good agreement, giving a value of polymerization of hydrogen cyanide of 377 cal. per gram, about 1-1/2 times the heat of vaporization.

The value for 1.5% water in hydrogen cyanide was chosen as an average value on the basis of several previous analyses.

CONCLUSIONS

Hydrogen cyanide is stable at or below room temperature, if it is inhibited with acid. The inhibitor content should be kept in the range of 0.1% expressed as sulfuric acid. The explosion of the laboratory hydrogen cyanide vaporizer can be attributed to loss of inhibitor (sulfur dioxide was being used) during the early periods of vaporization, followed by accelerating polymerization. The heavy insulation prevented the heat of polymerization from dissipating, resulting in an accelerating heat build-up, raising the temperature to or near to the critical of 184° C. Extremely rapid polymerization then occured, resulting in a very rapid rise in temperature and pressure and rupturing the container with explosive violence.

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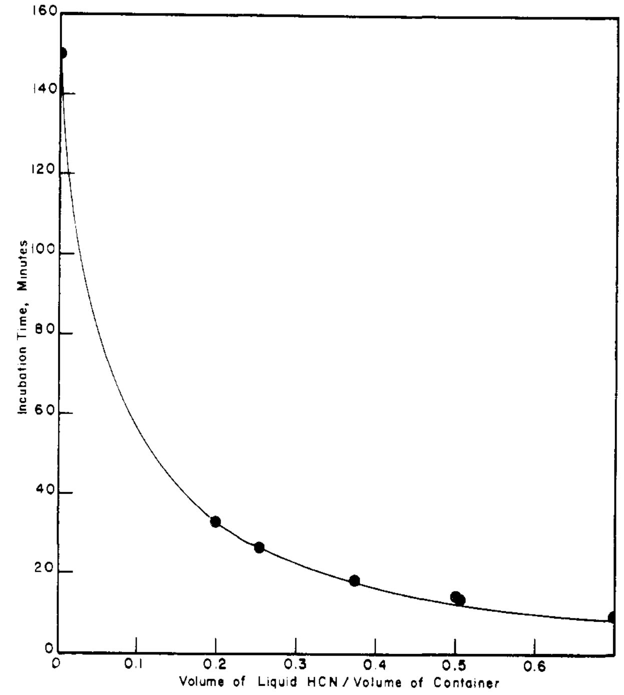

Figure 5. Effect of ratio, volume of liquid hydrogen cyanide charged/volume of container, on incubation time at 175° C.

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