

Sir William Ramsay

## 1904

In 1901-1902 Ramsay had been asked to advise the Indian government on the founding of a science institute and the institute was established in Bangalore with the help of the Government of Mysore and JN Tata. Ramsay suggested his student Morris Travers as a possible director for this institute and in 1906, Travers was appointed as the first director of the new Indian Institute of Science



Morris M. Travers (1862-1961)







Sir William Ramsay discovered neon, krypton, and xenon and received Nobel Prize in 1904. He also isolated helium which had been observed in the spectrum of the sun but had not been found on earth till then. In 1910 he also made and characterized radon. (1894 argon with Lord Raleigh) •The relative abundance of rare gases in the atmosphere decreases in the order Ar>Ne>He> Kr/Xe>Rn.

•Among the rare gases except for helium and neon all other rare gases have been made to undergo reactions leading to novel compounds.

•These compounds are neutral, anionic and cationic as well as where a rare gas acts as a donor ligand or the substituent on a rare gas compound acts as a ligand.

•Most of the rare gas compounds are endothermic and often oxidizing in nature.

•The stabilization of rare gas compounds have been mostly achieved by high electro negative substituents such as F, O, Cl or anions having high group electro negativities (e.g. teflate anion  $F_5$ TeO- E.N. 3.87)

•The very low bond enthalpy and high standard reduction potential of many of the rare gas compounds make them very strong oxidizers.  $KrF_2$  is the strongest oxidizing agent known so far with a higher  $E_0$  of 3.5 V compared to  $F_2$  ( $E_0$  2.87 V). The bond enthalpy of  $KrF_2$  is 49 kJ/mol compared to 154 kJ/mol of  $F_2$ .

•The high oxidizing strength of KrF<sub>2</sub> has been utilized for making high oxidation state metal complexes such as Au<sub>2</sub>F<sub>10</sub> and AgF<sub>3</sub>

•One of the most unstable of rare gas compounds known so far is HArF, the only covalent compound of argon which is stable only below 17 K (-256 °C). The shapes of most of the rare gas compounds comply with the VSEPR rules. Few exceptions are XeF<sub>6</sub>, XeO<sub>2</sub>, XeF<sub>8</sub><sup>2-</sup>

•The useful applications rare gases involve Xenon as an efficient inhalation anesthetic, as media for colored illuminating displays and fluorides especially  $XeF_2$  as an oxidizing and fluorinating reagent.

•Excimer lasers are ultraviolet lasers, commonly used in the production of microelectronic devices, semiconductor based integrated circuits, Lasik eye surgery, and micromachining. It typically uses a combination of a noble gas (argon, krypton, or xenon) and a reactive gas (fluorine or chlorine) which under electrical stimulation and high pressure, generates a pseudo-molecule (excimer) having only a transient existence and gives rise to Laser light in the UV region.

•Liquid helium is produced commercially for use in superconducting magnets such as those used in magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR).

Lord Raleigh in the journal Nature in 1892 in which he requested the readers of chemistry community to help him in explaining an observation while trying to determine the density of nitrogen. The excerpt from Nature **46**, 512–513 (1892) reads as follows.

am much puzzled by some recent results as to the density of nitrogen, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to two methods of preparation I obtain quite distinct values. The relative difference, amounting to about 1/1000 part, is small in itself; but it lies entirely outside the errors of experiment, and can only be attributed to a variation in the character of the gas.

In the first method the oxygen of atmospheric air is removed in the ordinary way by metallic copper, itself reduced by hydrogen from the oxide. The air, freed from  $CO_2$  by potash, gives up its oxygen to copper heated in hard glass over a large Bunsen, and then passes over about a foot of red-hot copper in a furnace. This tube was used merely as an indicator, and the copper in it remained bright throughout. The gas then passed through a wash-bottle containing sulphuric acid, thence again through the furnace over copper oxide, and finally over sulphuric acid, potash, and phosphoric anhydride.

In the second method of preparation, suggested to me by Prof. Ramsay, everything remained unchanged, except that the first tube of hot copper was replaced by a wash-bottle containing liquid ammonia, through which the air was allowed to bubble. The ammonia method is very convenient, but the nitrogen obtained by means of it was 1/1000 part lighter than the nitrogen of the first method. The question is, to what is the discrepancy due?"



Raleigh

Ramsey



Noble gas	Meaning/origin	Discoverer
Argon	The Lazy one / air	Raleigh and Ramsey
Helium	Helios- Sun / heating uranium mineral 'clevite'	Ramsey Cleve and Langlet
Krypton	The hidden one /air	Ramsey
Neon	The new one /air	Ramsey
Xenon	The stranger /air	Ramsey
Radon	/From decay of radium	Friedrich Ernst Dorn

However, the first evidence of helium was observed on August 18, 1868, as a bright yellow line with a wavelength of 587.49 nanometers in the spectrum of the sun detected by French astronomer Jules Janssen during a total solar eclipse in Guntur, India, initially assumed to be of sodium. In the same year, English astronomer Norman Lockyer observed a yellow line in the solar spectrum. He concluded that it was caused by an element in the sun unknown on Earth. Lockyer and the English chemist Edward Frankland named the element helium.

Abundance	Helium	Neon	Argon	Krypton	Xenon	Radon
Earth's						
atmosphere						(0.06_18)
(volume	5.20	18.20	9340.00	1.10	0.09	(0.00-10) $\times 10^{-19}$
fraction						× 10
in ppm)						

 Noble gases are colorless, odorless, tasteless, and nonflammable gases under standard conditions.

•Noble gases are widely used in different fields, from incandescent lighting to excimer lasers.

•Xenon is used as an anesthetic because of its high solubility in lipids, which makes it more potent than the usual nitrous oxide, and because it is readily eliminated from the body, which helps in faster recovery.

•Xenon finds application in medical imaging of the lungs through hyperpolarized MRI.

•XeF<sub>2</sub> is a good fluorinating agent

Gas	Approx. price (USD/m <sup>3</sup> )
Helium (ind. grade)	4.20–4.90
Helium (lab. grade)	22.30–44.90
Argon	2.70-8.50
Neon	60–120
Krypton	400–500
Xenon	4000–5000

### The Yost and Kaye experiments on exploring reactivity of xenon done on the



### advice of Linus Pauling



Yost

### **Linus Pauling**

Passing electric discharge on a mixture of Xenon and large excess of fluorine gas in a special quartz reactor vessel with copper electrodes



Fig. 1. The copper electrical discharge vessel used by Yost and Kave for the reaction of xenon with fluorine (see text).

#### Yost and Kaye Experiments

#### CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA

GATES CHEMICAL LABORATOR

September 13,1932

Dear Fred:

I should like to do some work (with Postanon Voit) in an attempt to prepare intain compounds of Xemon suggested by theoretical arguments. No doubt your Article remon is precisions; if however, you could lend is 10 cc. on so (of not necessarily sure stuff), we would try to inturn it to you either as such or sin sung compared (I hope), and we would be properly grateful, If this is asking too much , on if you can't lend it, could you give us advice as to when we might possibly obtain some? We were released to get your letter & prictures some time ago, and hope our card also arrived. Next christings we'll need a Jouger could, with room for kinda, now 13 weeks old We hope you are getting along well. Sincenely . finis Banking

**AN ATTEMPT TO PREPARE A** CHLORIDE OR FLUORIDE OF XENON Don M. Yost, Albert L. Kaye J. Am. Chem. Soc., **1933**, 55 (9), pp 3890-3892 **DOI:** 10.1021/ja01336a506 Publication Date: September 1933

> Yost- CalTech Kaye- MIT

By means of quartz "break-offs" a mixture of some 600 mm. of fluorine and 30 mm. of xenon was prepared in an all-quartz apparatus provided with copper electrodes. On condensing the mixture in a side tube at -210' no visual evidence of the existence of anything except liquid fluorine and solid xenon was observed. When the refrigerant was removed the fluorine boiled away rapidly, leaving a volatile white solid with all the properties of xenon. A high voltage (30 k.v.) discharge was then passed through the mixed gases for varying intervals of time. The contents of the apparatus were condensed out frequently, but the appearance and properties were no different from those observed before applying the discharge. It was noted that the side tube was appreciably attacked after some time, and this might be due to the action of a reactive xenon fluoride. It cannot be said that definite evidence for compound formation was found. It does not follow, of course, that xenon fluoride is incapable of existing. It is known, for example,, that nitrogen and fluorine do not combine in an electrical discharge, but when prepared indirectly nitrogen trifluoride is a very stable compound

J. Am. Chem. Soc., 1933, 55 (9), pp 3890-3892

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA

1201 - E - Cali

July 12, 1933

Dr. F. J. Allen, Chemistry Department, Purdue University, Lafayette, Ind.

Dear Fred:

At last I can send you some information regarding the xenon experiments, which Dr. Yost has been carrying on, inestuch as he is thoroughly experienced in the chemistry of the halogens. He found that he could not prepare a contound of menon with either chlorine or fluorine by any of the means that he tried, and he has now given up the investigation. He and his student, Raye, have sent a note on the experiments to the Journal of the American Chemical Society, in which they thank you for providing the xenon. I am sorry that the experiments have turned out in this way since I felt confident that genon would combine with fluorine, at any rate. Yost obtained some rod crystals, which he at one time thought contained xenon, but which he later decided were the pink form of hydrogen chloride.

My wife and I have just visited Oregon, where we saw Prof Fulton, Gilbert, and a lot of other people. We had such a good time that we are thinking of spending our vacation there next year.

With best wishes to you and Mrs. Allen, I am

Very sincerely yours,

Lino Paulino

1.P:M

P.S. I want to thank you very much for providing the xenon. If there is anything that I can do for you, let me know and I shall try to do it.

### Neil Bartlett and the discovery of a young Asst Professor

### The discovery of the first noble gas reaction

In March of 1962, Bartlett set up a glass apparatus containing PtF<sub>6</sub>, a red gas in one container and xenon, a colorless gas in an adjoining container, separated by a seal. Here's his recollection of the ensuing experiment, which he conducted while working alone in his laboratory: "Because my co-workers at that time (March 23, 1962) were still not sufficiently experienced to help me with the glassblowing and the preparation and purification of PtF<sub>6</sub> [platinum hexafluoride] necessary for the experiment, I was not ready to carry it out until about 7 p.m. on that Friday. When I broke the seal between the red PtF<sub>6</sub> gas and the colorless **xenon gas**, there was an immediate interaction, causing an orange-yellow solid to precipitate. At once I tried to find someone with whom to share the exciting finding, but it appeared that everyone had left for dinner!"

The reaction took place at room temperature "in the twinkling of an eye" and was "extraordinarily exhilarating," recalls Bartlett.





#### **Bartlett's Conclusion**

$$O_2 + PtF_6 \longrightarrow [O_2]^{\odot} [PtF_6]^{\odot}$$
  
|  
 $IP = 12.2 eV$ 

Xe + PtF<sub>6</sub> 
$$\longrightarrow$$
 [XeF] <sup>$\odot$</sup>  [PtF<sub>6</sub>] <sup>$\odot$</sup>   
|  
|P = 12.1 eV

Pages from Niel Bartlett's Laboratory Notebook





Neil Bartlett and Rudolf Hoppe: The race to become the first to make xenon compounds



MILESTONE When platinum hexafluoride, a red gas (left), is allowed to mix with a large molar excess of xenon, the immediately formed product is a yellow solid with the composition XePtF<sub>6</sub> (right)—the first recognized compound of a noble gas.



**STARRY REACTION** UV irradiation of a 1:1 mixture of gaseous xenon and fluorine at McMaster University yields crystals of XeF<sub>2</sub> that adhere to the inside of the reaction vessel.

Bartlett's reaction to make the first Xenon fluorine compound

$$O_2 + PtF_6 \longrightarrow [O_2]^+ [PtF_6]^-$$

I<sup>st</sup> Ionization potential of Xe (12.1 eV and  $O_2$  12.2 eV)





phase :

**Distorted Oh** 





<sup>129</sup>Xe and <sup>19</sup>F NMR spectroscopy indicates that in solution the compound assumes a tetrameric structure: four equivalent xenon atoms are arranged in a tetrahedron surrounded by a fluctuating array of 24 fluorine atoms that interchange positions





Na, K, Rb,Cs F NO, NO<sub>2</sub> F





 $XeO_3$  is a very powerful oxidizing agent, and liberates oxygen from water slowly (and xenon), accelerated by exposure to sunlight. It is dangerously explosive upon contact with organic materials. Above 25 C it is prone to violent explosion and when it detonates, it releases xenon and oxygen gas.

$$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2H_2O + 2Na_2SO_4$$

 $XeO_4$  is an yellow <u>crystalline</u> solid that is stable below -35.9 °C; above that temperature it is very prone to exploding and decomposing into elemental xenon and oxygen (O<sub>2</sub>)

### **Oxides of Xenon**

Oxide	Xe=O	XeO <sub>2</sub> (2011)	XeO <sub>3</sub> (1982)	XeO <sub>4</sub> (1964)
stability	Unstable,	Stable below -78 °C	Stable below 25 °C	Stable below -36 °C
	not known			
shape	NA	Predicted: bent	Triangular pyramid	tetrahedral
		Actual: extended		
		square planar		
Heat of	NA	487 kj/mol	402 kj/mol	643 kj/mol
formation		endothermic	endothermic	endothermic
Preparation		$XeF_6 + H_2O$	XeF <sub>6</sub> + HOP(O)F <sub>2</sub>	$Na_2XeO_6 + H_2SO_4$





o<sup>™</sup>Xe<sup>™</sup>O

1.74-1.77 Å

1.73 Å





The reaction of hexahydroxytellurium  $Te(OH)_6$  with fluorosulfonic acid results in a very useful acid known as the teflic acid  $F_5TeOH$  (m.p. 40 °C, b.p. 60 °C). The  $F_5TeO$ - group is well suited for stabilization of high valent strong oxidant centers and tends to provide stable compounds that have fluorine analogues. This group is predicted to have a very high group electro negativity and calculations predict it to be in the range of 3.87-3.88 (Allred- Rochow scale)









- XeF<sub>2</sub>, XeF<sup>+</sup> and Xe<sub>2</sub>F<sub>3</sub><sup>+</sup> salts, XeF<sub>3</sub><sup>-</sup>
  - XeF<sub>4</sub>, XeF<sub>5</sub><sup>-</sup> salts, XeOF<sub>2</sub>
  - XeF<sub>6</sub>, XeF<sub>5</sub><sup>+</sup>, XeF<sub>7</sub><sup>-</sup> and Xe<sub>2</sub>F<sub>13</sub><sup>-</sup> salts, XeO<sub>3</sub>, XeOF<sub>2</sub>
    - $XeO_4$ ,  $H_4XeO_6$ ,  $XeO_6^4$ -salts



The first tetravalent organoxenon compound, [C<sub>6</sub>F<sub>5</sub>XeF<sub>2</sub>][BF<sub>4</sub>], was synthesized in 2004. So far, more than one hundred organoxenon compounds have been prepared

#### **Krypton difluoride**

$$\operatorname{Kr} + F_{2}(1:4) \longrightarrow \operatorname{Kr} F_{2}$$

#### liquified mixture

Colorless solid. Decomposes above 250 K . Lowest average bond energy of any known fluoride. Therefore the strongest oxidizing agent Even stronger than  $F_2$ . Linear molecule with a Kr-F bond distance of 1.89Å

$$7 \text{KrF}_{2} + 2 \text{Au} \longrightarrow 2 \text{KrF}^{+} \text{AuF}_{6}^{-} + 5 \text{ Kr}$$

$$2 \text{KrF}^{+} \text{AuF}_{6}^{-} \longrightarrow \text{Au}_{2}\text{F}_{10} + 2 \text{Kr} + \text{F}_{2} \quad \text{Gold (V) fluoride}$$

$$3 \text{KrF}_{2} + 2 \text{Ag} \longrightarrow 2 \text{AgF}_{3} + 3 \text{ Kr} \quad \text{Silver (III) fluoride}$$

Bond	Bond enthalpy
Xe-F	130.8 kj/mol
Xe-O	84 kJ/mol
Kr-F	49 kj/mol



Markku Räsänen <u>University of Helsinki</u>

### First and only Argon compound HArF

This chemical was synthesized by mixing argon and hydrogen fluoride on caesium iodide surface at 8 K (–265 °C), and exposing the mixture to ultraviolet radiation. This caused the gases to combine.

The discovery of this first <u>argon</u>compound is credited to a group of Finnish scientists, led by Markku Räsänen. On 24 August 2000, in the journal *Nature*, they announced their discovery of argon fluorohydride

The infrared spectrum of the resulting gas mixture shows that it definitely contains chemical bonds, albeit very weak ones; thus, it is argon fluorohydride, and not a supermolecule or a mixture of argon and hydrogen fluoride. Its chemical bonds are stable only if the substance is kept at temperatures below 17 K (–256 °C); upon warming, it decomposes into argon and hydrogen fluoride.

Khriachtchev, Leonid; Mika Pettersson; Nino Runeberg; Jan Lundell; Markku Räsänen (24 August 2000). <u>"A stable argon compound"</u>.*Nature*. **406** (6798): 874–876.

Au-Xe = 273-275 pm



Konrad Seppelt

2000

First metal-xenon compound where xenon acts as a ligand



The salt is formed from  $Au^{3+}$ , dissolved in HF/SbF<sub>5</sub>, in the presence of Xenon gas as a mild reductant

Konrad Seppelt discovers the first metal-xenon compound where xenon acts as a ligand achieved by reduction of  $AuF_3$  with xenon. The  $AuXe_4^{2+}(Sb_2F_{11})_2$  complex had a square planar gold with a Au-Xe bond distance of 274 pm. Bonding is of sigma donor type

$$AuF_3 + 6Xe + 3H^+$$
 — [AuXe<sub>4</sub>]<sup>2+</sup> + Xe<sub>2</sub><sup>+</sup> + 3HF

### More Gold-Xenon Complexes









Bond	Bond enthalpy
F-F	154 kJ/mol
1-1	149 kJ/mol
Xe-F	130.8 kj/mol
Xe-O	84 kJ/mol
Kr-F	49 kj/mol

$$3 \text{ KrF}_2 + \text{Xe}$$
  $\longrightarrow$  XeF<sub>6</sub> + 3Kr

### KrF<sub>2</sub> to Kr 3.5 V

	Reduction Half-Reaction		E° (V)	
Stronger	$F_2(g) + 2e^-$	$\rightarrow$ 2 F <sup>-</sup> (aq)	2.87	Weaker
oxidizing	H2O2(aq) + 2H*(aq) + 2e-		1.78	reducing
agent	$MnO_{4}(aq) + 8 H^{+}(aq) + 5 e^{-1}$	$\longrightarrow$ Mn <sup>2+</sup> (aq) + 4 H <sub>2</sub> O(1)	1.51	agent
	$Cl_2(g) + 2e^-$	$\longrightarrow 2 Cl^{-}(aq)$	1.36	
1	$Cr_2O_7^{2^+}(aq) + 14 H^+(aq) + 6 e$	$\rightarrow 2 \operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2O(1)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^-$	$\rightarrow 2 H_2O(I)$	1.23	
	Br <sub>2</sub> (aq) + 2 e <sup>-</sup>	$\rightarrow$ 2 Br <sup>-</sup> (aq)	1.09	
	$Ag^{+}(aq) + e^{-}$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^{-}$	$\longrightarrow$ Fe <sup>2+</sup> (aq)	0.77	
	O2(g) + 2 H+(aq) + 2 e-	$\longrightarrow$ H <sub>2</sub> O <sub>2</sub> (aq)	0.70	
	l <sub>2</sub> (s) + 2 e <sup>-</sup>	$\longrightarrow 2 I^{-}(aq)$	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^{-1}$	> 4 OH <sup>-</sup> (aq)	0.40	
	Cu <sup>2+</sup> (aq) + 2 e <sup>-</sup>	→ Cu(s)	0.34	
	Sn <sup>4+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow$ Sn <sup>2+</sup> (aq)	0.15	
	2 H*(aq) + 2 e-	$\longrightarrow$ H <sub>2</sub> (g)	0	
	$Pb^{2+}(aq) + 2e^{-}$	> Pb(s)	- 0.13	
	Ni <sup>2+</sup> (aq) + 2 e <sup>-</sup>	→ Ni(s)	- 0.26	
	Cd <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow$ Cd(s)	- 0.40	
	$Fe^{2+}(aq) + 2e^{-}$	→ Fe(s)	- 0.45	
	$Zn^{2+}(aq) + 2e^{-}$	$\rightarrow$ Zn(s)	- 0.76	
	2 H <sub>2</sub> O(/) + 2 e <sup>-</sup>	$\longrightarrow$ H <sub>2</sub> (g) + 2 OH <sup>-</sup> (aq)	- 0.83	
	$AI^{3+}(aq) + 3e^{-}$	$\longrightarrow$ Al(s)	- 1.66	
Weaker	$Mg^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Mg(s)	- 2.37	Stronger
oxidizina	Na <sup>+</sup> (aq) + e <sup>-</sup>	→ Na(s)	- 2.71	reducing
agent	Li <sup>+</sup> (aq) + e <sup>-</sup>	$\longrightarrow$ Li(s)	- 3.04	agent
NATIONAL DESIGNATION OF THE PROPERTY OF THE PR	Xenon			29.2590 03 <b>7</b> )

### TABLE 17.1 Standard Reduction Potentials at 25 °C

 $H_4XeO_6 + 2H^+ + 2e^- \rightleftharpoons XeO_3 + 3H_2O$  2.38

  $XeF_2 + 2H^+ + 2e^- \rightleftharpoons Xe(g) + 2HF$  2.2

  $XeO_3 + 6H^+ + 6e^- \rightleftharpoons Xe(g) + 3H_2O$  2.1

# **Excimer Lasers**

Rare gas compounds along with halogens are used to make a unique type of laser known as eximer laser or sometimes as exciplex laser. The excimer laser uses reactive gases, such as chlorine and fluorine, mixed with inert gases, such as argon, krypton and xenon. When electrically excited, the gas mixture emits energetic pulses of ultraviolet light of a specific frquency, which can make very precise, minute changes to irradiated material, such as polymers.

Two important and path-breaking applications of excimer lasers were independently discovered by two research groups in America in 1981-82 and in both, the leading scientists were persons of Indian origin. In 1981, Rangaswamy Srinivasan working at the IBM TJ Watson Research Center discovered that an ultraviolet excimer laser could be used to etch a living tissue without causing any thermal damage to surrounding areas. He named the phenomenon Ablative Photo-Decomposition (APD). Three years later, Rangaswamy collaborated with an ophthalmic surgeon to use a ArF (193nm) excimer laser to reshape the cornea, to arrive at a novel method of eye surgery called Lasik surgery (laser-assisted in situ keratomileusis) which has since then helped millions of people a permanent alternative to eye glasses or contact lenses.

Excimer rare gas/ rare gas halogen combination	Wavelength of laser produced	Relative power mW
Xe <sub>2</sub> *	172 & 175 nm	NA
ArF	193 nm	60
KrCl	222 nm	25
KrF	248 nm	100
XeBr	282 nm	NA
<u>XeCl</u>	308 nm	50
XeF	351 nm	45

The other path-breaking discovery was made by Dr Kanti Jain (B.Tech degree holder from IIT Kharagpur and Ph.D in Elec. Engg from University of Illinois and post doc from MIT). The most widespread industrial application of excimer lasers has been in deep ultraviolet photolithography, a critical technology used in the manufacturing of microelectronic devices (integrated circuits). In a pioneering development in 1982, deep-UV excimer laser lithography was proposed and demonstrated at IBM by Kanti Jain.