Miscibility and Compatibility of Some Liquefied and Solidified Gases at Low Temperatures

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The miscibility and compatibility characteristics of selected liquefied and solidified gases are presented, and the reactions at low temperatures between the solutions of some noncompatible gases are described.

Very little information is available, at the present time, on the miscibility of liquefied gases at low temperatures and on the compatibility of various liquefied or solidified gases at cryogenic conditions.

The experimental observations reported herein have been accumulated in our laboratory during many years of work. The tests performed had purely applied purpose; thus, the observations made are not sufficient for extensive interpretations. However, as experimental facts, they may provide useful information for certain fields of science and industry.

Some of the investigated systems are extremely hazardous and may explode at slightest provocation. The danger characteristics of such systems are indicated in each particular case. These mixtures must be (and have been) handled with great care behind safety shields of sufficient strength (or behind barricades).

EXPERIMENTS

The mixing tests were made to find the temperature

Table I. Miscibility Behaviour of Liquefied Gases at Low Temperatures

(Pressure of the gaseous phase, ≦1 atm)[a]

Liquefied gas	Mixes homogeneously in molar ratio of 1:1		Forms two separate layers		Dissolves
	With	@ ° K	With	@ ° K	
Argon, Ar	N_2	77	O_3	85	30 Mol % of Kr
Mp = 84.0° K	CO	77	C_3H_8	87	@ 87.5° K
Bp = 87.5° K	F_2	77	C_3H_6	87	
d = 1.4 g/cm^3 @ bp	OF_2	77	CHF_3	88	
	NF_3	77	C_2H_4	90	
	O_2	85			
	C_2H_6	87			
	CF_4	88			
	CH_4	90			
Nitrogen, N_2	F_2	77	O_3	77	18 Mol % of Kr
Mp = 63.3° K	OF_2	77	O_2F_2	77	@ 77° K
Bp = 77.4° K	CO	77	C_2H_6	77	
d = 0.808 g/cm^3 @ bp	Ar	77	C_3H_8	77	
	CH_4	77	C_3H_6	77	
	$CClF_3$	77	CHF_3	77	
	O_2	78			
Oxygen, O_2	N_2	77	ClF	90	6.9 Mol % of O_3
Mp = 54.8° K	F_2	77	ClO_3F	90	@ 77° K
Bp = 90.2° K	NF_3	77	CCl_2F_2	90	17.6 Mol % of O_3
d = 1.1416 g/cm^3 @ bp	CO	77	CHF_3	90	@ 90° K
	Ar	85	C_2H_6	90	28 Mol % of Kr
	CF_4	90	C_3H_8	90	@ 77° K
	CH_4	90	C_3H_6	90	<1% of ClF @ 90° K
	OF_2	90	O_2F_2	90	Significant amount of
	Kr	90	Xe	90	N_2F_4 @ 90° K
	O_3	94			
Ozone, O_3	F_2	77	N_2	77	32.8 Mol % of O_2
Mp = 80.7° K	OF_2	77	Ar	85	@ 90° K
Bp = 161.3° K	CO	77^{b}			15.7 Mol % of N_2
d = 1.574 @ 90° K	NF_3	90			@ 77° K
	CH_4	90^{b}			
	$CClF_3$	90			
	O_2	94			
	ClO_3F	116			
	O_2F_2	120^{c}			
	CCl_2F_2	130			
	ClF_3	195			
Fluorine, F_2	N_2	77	O_2F_2	77	29 Mol % of Kr
Mp = 55.2° K	OF_2	77	ClF_3	85	@ 77° K
Bp = 85.2° K	O_2	77	Xe	85	47 Mol % of Kr
d = 1.505 g/cm^3 @ bp	O_3	77			@ 90° K
	Ar	77			
Oxygen difluoride, OF_2	N_2	77	CO_2	77	~30 Mol % of Kr
Mp = 49.4° K	F_2	77	C_2H_4	77^{d}	@ 77° K
Bp = 127.9° K	NF_3	77	Xe	90	Traces of O_2F_2
d = 1.719 @ 90° K	CO	$77^{b,c}$	O_2F_2	135	@ 135° K
	O_3	77	ClF_3	140	~0.05% of ClF_3
	Ar	85			@ 140° K
	O_2	90			
Oxygen difluoride, OF_2	CF_4	90			
	$CClF_3$	90			
	CH_4	90^{b}			
	N_2F_4	110			
	Kr	120			
	ClF	125			
Dioxygen difluoride, O_2F_2	CCl_2F_2	116	N_2	77	~20% of SiF_4
Mp = 109.7° K	CCl_3F	116	F_2	77	@ 150° K
Bp = 216° K (dec.)	O_3	120^{c}	O_2	90	~10% of HF
d = 1.736 g/cm^3	N_2F_2	120	CF_4	90	@ 186° K
@ 116° K	ClO_3F	127	N_2F_4	130	
	NO_2F	195^{f}	NF_3	130	
	ClF_3	180^{f}	OF_2	135	
			C_3F_8	140	
Nitrogen trifluoride, NF_3	O_2	77	O_2F_2	130	
	OF_2	77	ClF_3	140	
Mp = 64.7° K	Ar	85			
Bp = 144 ° K	O_3	90	HF	140	
d = 1.830 g/cm^3	$CClF_3$	90	ClF	150	
@ 77° K	CF_4	90			
Tetrafluorohydrazine, N_2F_4	OF_2	110	O_2F_2	130	
	CCl_2F_2	130			
Mp = 105° K					
Bp = 200° K					
d = 1.5 @ 173° K					
Nitryl fluoride, NO_2F	$CClF_3$	90			
Mp = 107.2° K	O_2F_2	195^{f}			
Bp = 200.8° K					
d = 1.492 g/cm^3 @ bp					
Chlorine fluoride, ClF	OF_2	125	O_2	90	
Mp = 117.6° K	ClO_3F	160	NF_3	150	
Bp = 173.1° K	C_3F_8	160	HF	173	
d = 2.136 g/cm^3 @ mp			ClF_3	174	
Chlorine trifluoride, ClF_3	O_2F_2	180^{f}	CCl_2F_2	125	
Mp = 196.84° K	ClO_3F	195	NF_3	140	
Bp = 285.10° K	HF	195	OF_2	140	
d = 2.125 g/cm^3 @ mp	O_3	195^{g}	ClF	174	
= 1.854 g/cm^3 @ bp			F_2	185	
			$CClF_3$	190	
			(C_2F_5)-NC_3F_7	195	
			CF-15	195	
			C_3F_8	235	
Chlorine pentafluoride, ClF_5	CCl_2F_2	180	N_2	77	~17.5 Mol % O_3
	ClF	185	F_2	77	@ 140° K
Mp = 171° ± 1° K	ClF_3	190	OF_2	90	
Bp = 260.3° K			O_2	90	
d = 2.16 g/cm^3					
@ 175° K					

(Continued on next page)

Table I. (*Continued*)

Perchloryl fluoride,	O_3	116	O_2	90	
ClO_3F	$CClF_3$	125	O_3	90	
Mp = 127.2° K	O_2F_2	127			
Bp = 226.4° K	ClF	160			
d = 1.8 g/cm^3 @ 195° K	SF_4	180			
= 1.694 g/cm^3 @ bp	SF_6	195			
	ClF_3	195			
	C_4H_{10}	195			
Hydrogen fluoride, HF	ClF_3	195	C_3F_8	125	>16 Wt % of ClF
Mp = 190.0° K			NF_3	140	@ 195° K
Bp = 292.7° K			ClF	173	>15 Wt % of HN_3
d = 1.0015 g/cm^3					@ 195° K[g]
@ 273° K					>12 Wt % of O_2F_2
= 1.1975 g/cm^3					@ 195° K
@ 195° K					>3 Wt % of O_3
= 0.991 g/cm^3					@ 195° K
@ bp					>0.35 Wt % of HNF_2
					@ 195° K
					>0.12 Wt % of OF_2
					@ 195° K
Dichlorodifluoro-	O_2F_2	116	O_2	90	~20 Wt % of ClF
methane, CCl_2F_2	C_2H_4	116	SiF_4	130	@ 125° K
(Freon 12)	N_2F_4	130	HN_3	200[g]	~35 Wt % of ClF_3
Mp = 115.2° K	O_3	130	NH_3	240	@ 200° K
Bp = 243.4° K	SF_4	195			
d = 1.6156 g/cm^3					
@ 195° K					
= 1.4882 g/cm^3 @ bp					
Monochlorotrifluoro-	N_2	77	Cl_2	90	>10 Mol % of
methane, $CClF_3$	OF_2	77	SiF_4	125	$CH_2{:}CF_2$ @ 90° K
(Freon 13)	O_2	90	ClF_3	190	~12 Wt % of ClF
Mp = 92.2° K	O_3	90			@ 90° K
Bp = 191.8° K	NF_3	90			~ 1 Wt % of ClF_3
d = 1.726 g/cm^3	NO_2F	90			@ 195° K
@ 163° K	O_2F_2	116			>10 Mol % of
	ClO_3F	125			CH_3OCH_3 @ 90° K
Carbon tetrafluo-	CO	77	O_2F_2	90	~11 Wt % of O_3
ride, CF_4	NF_3	77	CO_2	90	@ 90° K
Mp = 89 ° K	OF_2	77	BF_3	90	>1 Mol % of O_4F_2
Bp = 145 ° K	Ar	88	SiF_4	90	@ 90° K
d = 1.96 g/cm^3 @ 90° K	O_2	90	C_2H_4	145	Small amount of
= 1.6447 g/cm^3	CH_4	112	HBr	120	O_2F_2 @ 90° K
@ 143° K					
Trifluoromethane, CHF_3	C_3H_6	90	N_2	77	
Mp = 110.2° K	C_3F_8	90	CO	77	
Bp = 191.0° K			Ar	88	
			O_2	90	
			C_2H_6	90	
			C_3H_8	90	
			CH_4	102	
Fluoropropane, C_3F_8	C_2H_6	90	CH_4	90	
Mp = 90° K	C_3H_8	90	O_2F_2	140	
Bp = 235° K	C_3H_6	90	HF	195	
	CHF_3	90	ClF_3	235	
	ClF	160			
Sulfur tetrafluoride, SF_4	ClO_3F	180			
Mp = 152° K	CCl_2F_2	195			
Bp = 236° K					
d = 1.934 g/cm^3					
@ 195° K					
= 1.8061 g/cm^3 @ bp					
Carbon monoxide, CO	Ar	77	C_3H_8	77	
Mp = 66° K	N_2	77	C_3H_6	77	
Bp = 81.7° K	O_2	77	CHF_3	77	
d = 0.793 g/cm^3 @ bp	O_3	77[e]	C_2H_6	83	
	OF_2	77[b,c]			
	CF_4	77			
	CH_4	77			
Methane, CH_4	N_2	77	C_3F_8	90	~10 Wt % of C_2H_4
Mp = 85.7° K	CO	77	CHF_3	102	@ 90° K
Bp = 111.6° K	Ar	90			
d = 0.415 g/cm^3	O_2	90			
@ 109° K	O_3	90[b]			
	C_2H_6	90			
	C_3H_8	90			
	C_3H_6	90			
	OF_2	90[b]			
	CF_4	112			
Ethane, C_2H_6	Ar	87	N_2	77	
Mp = 101° K	CH_4	90	CO	83	
Bp = 184.6° K	C_3F_8	90	O_2	90	
d = 0.561 g/cm^3	C_3H_8	195	CHF_3	90	
@ 173° K	C_3H_6	195			
Propane, C_3H_8	CH_4	90	N_2	77	
Mp = 85.5° K	C_3F_8	90	CO	77	
Bp = 231.1° K	C_2H_6	195	Ar	87	
d = 0.5853 g/cm^3	C_3H_6	195	O_2	90	
@ 229° K			CHF_3	90	
Propylene, C_3H_6	CH_4	90	N_2	77	
Mp = 88.0° K	CHF_3	90	CO	77	
Bp = 225.5° K	C_3F_8	90	Ar	87	
d = 0.6095 g/cm^3 @ bp	C_2H_6	195	O_2	90	
	C_3H_8	195			
Ethylene, C_2H_4	CCl_2F_2	116	Ar	90	Small amount of
Mp = 103.8° K			OF_2	77[d,e]	CH_4 @ 90° K
Bp = 169.3° K			CF_4	145	
d = 0.566 g/cm^3 @ bp					

[a] In a few cases the pressure was slightly higher than 1 atm abs. [b] Mixture explodes at slight provocation and at higher temperature. [c] Mixture explodes at a temperature slightly above 120° K. [d] A suspension of solid C_2H_4 in liquid OF_2 exploded violently at a temperature slightly above 77° K. [e] The mixture is very sensitive to friction; using Rasching rings, for example, caused violent explosion @ 77° K. [f] Thermal decomposition of O_2F_2 noticed. [g] The solution must be handled with care, it is potentially explosive. [h] Ethylene is soluble in a mixture of 25% (liquid by volume) of CF_4 and 75% of $CClF_3$ at 90° K in amounts up to 5 mol %.

at which two given liquefied gases mix homogeneously in equimolar amounts. The lowest temperature applied was 77° K.

The experimental procedure was as follows: One component (measured as a gas) was condensed in a graduate tube cooled in a Dewar flask containing boiling liquid nitrogen (*T*, 77° K). The second component (also measured in the gas phase) was then introduced into the same tube in small portions and mixed with the first component.

The mixing was achieved either by simple shaking of the tube or by means of a hand-operated magnetic stirrer.

If at 77° K the amount of liquefied gas added dissolved completely in the liquefied solvent gas, new portions were introduced up to the equimolar amounts. If, however, the introduced quantity of gas did not dissolve completely, or solidified, the temperature of the cooling bath was raised to the point where the equimolar amounts of gases did mix homogeneously. However, the temperature was never raised over the point where the pressure of the gaseous phase of the mixture surpassed 1 atm abs (with few exceptions).

At the same time, observations were made on the compatibility of the substances tested. The mixtures were kept at the indicated temperatures under visual observation for at least 1 hr (in some cases, for several days), and the pressure of the gaseous phase of the mixtures was registered.

Some of the liquefied or solidified gases were not compatible when tested in concentrated form. Thus, the reactions of these substances were investigated using dilute solutions (or suspensions) in suitable solvents at low temperatures.

Boiling liquid oxygen was used for baths with the temperature of 90° K. Mixtures of liquid oxygen with liquid nitrogen were used for baths with temperatures between 77° and 90° K. Freon 13 and 12, or their mixtures (cooled with liquid nitrogen to desired temperature), were used for baths with temperatures over 90° K.

The bath temperatures were measured with a pentane thermometer with an accuracy of ±1° K. The accuracy of the thermometer was checked by measuring the temperatures of melting ice, melting dichlorodifluoro methane, and boiling oxygen.

All the gases used (except O_3 and O_2F_2) were commercial products of the highest available purity. Most of the gases were supplied by the Matheson Gas Products, East Rutherford, N. J. Their purity is described in the Matheson Gas Catalog. They were additionally purified by fractional distillation.

The oxygen difluoride was obtained from the Baton Rouge Development Laboratory, General Chemical Division, Allied Chemical Corp. It contained originally 97.7% by weight of OF_2, 1.75% of O_2, and 0.55% of CO_2. Before use, it was purified in our laboratory by fractional distillation. The purity of the OF_2 (and other gases) was checked by infrared spectroscopy.

Ozone and dioxygen difluoride were prepared in our laboratory.

MISCIBILITY

The experimentally determined temperatures at which two given liquefied gases do mix homogeneously in equimolar amounts are presented in Table I. In all cases presented in Table I, there were no visible reactions between the components *at the indicated temperatures.* One must emphasize, however, that the observation time was comparatively short and that the components used were pure. In the presence of catalytically acting impurities and at higher temperatures, some of the combinations tested may react rather slowly or violently. Some of the mixtures shown in Table I are very sensitive and dangerous (as indicated in the corresponding footnotes).

For example, the pure 100% ozone, as well as its concentrated mixtures (even with the inert gases), is very dangerous. The mixtures of liquid ozone with liquefied oxidizable gases and with O_2F_2 are extremely sensitive and may explode at the slightest provocation.

The mixtures of liquid oxygen difluoride with liquid methane, carbon monoxide, and other combustible substances, detonate spontaneously if the temperature is raised slightly higher than indicated in Table I. Mixtures containing O_2F_2 may explode without apparent known provocation.

The dangerous systems have been prepared, observed, handled, and stored with great care behind safety shields (or barricades) of sufficient strength. Remotely controlled valves were employed; the stopcocks were operated by means of elongated handles from behind the safety shields.

The values presented in Table I are proximate, and small deviations are possible.

For ready reference, selected values of the melting and boiling points, and, in many cases, also the densities of the liquefied gases are given. These values have either been adapted from literature or determined in our laboratory.

COMPATIBILITY

All the combinations of substances presented in Table I appeared to be compatible—i.e., no reaction was noticed between the components of the mixtures tested in the course of observation. The possibility of violent reaction of some of these mixtures is indicated in the footnotes.

Some other substances were not compatible. In most cases, these substances reacted violently when used in the concentrated form. Thus, the reactions of these substances were investigated using dilute solutions (or suspension).

O_3 + C_2H_4. Liquid ozone exploded at contact with solid ethylene at 90° and 77° K. However, when a 9 mol % solution of O_3 in CF_4 was slowly added to a 3-mol % solution of C_2H_4 in a CF_4 + $CClF_3$ mixture at 90° K, the reaction proceeded without violence. The main reaction product was the ethylene ozonide, $C_2H_4O_3$. In several experiments the reaction product exploded after being warmed to room temperature.

O_3 + CH_2CHCl. When liquid ozone was added to the concentrated liquid vinyl chloride at a temperature close to its melting point (113.5° K), a violent explosion occurred. However, when a suspension of solid CH_2CHCl (taken in amounts of about 1 mol % in a mixture of 25% of $CClF_3$ + 75% CF_4) was mixed with a 1-mol % solution of ozone (in the same solvent) at 90° K, the reaction proceeded smoothly. A suspension was used because of a very low solubility of the CH_2CHCl in Freons. Only about 12 mol % of CH_2CHCl ($\sim$9 wt %) is soluble in a mixture of 37.5% of CF_4 + 63.5% of $CClF_3$ (liquid by volume) at 150° K. The main reaction product had an infrared spectrum characteristic for an ozonide. Thus, it is believed that the product was CH_3ClO_3. The product was extremely sensitive and exploded at room temperature from a slight impact on the tube.

O_3 + CH_2CHF. The concentrated liquid vinyl fluoride (at a temperature close to its melting point) caused an explosion at contact with the concentrated liquid ozone. On the other hand, the solutions containing 1.35 mol % of CH_2CHF and 1 mol % of O_3 in a mixture of 20% of $CClF_3$ + 80% of CF_4 reacted smoothly at 90° K. The main reaction product had an infrared spectrum characteristic for an ozonide. It is believed that the product was $C_2H_3FO_3$. The product polymerized at room temperature and exploded at slight warming.

O_3 + CH_2CF_2. 1,1-Difluoroethylene and ozone taken in form of 2–4-mol % solutions reacted slowly at temperatures of 140–160° K. The infrared spectrum of the main reaction product suggested that the ozonide, $CH_2CF_2O_3$, did form. The product was stable at room temperature but exploded violently from a spark initiated by a high-frequency induction coil (leak tester).

O_3 + HBr. Concentrated ozone explodes in contact with the solid HBr at 90° K. A dilute solution of O_3 in CF_4 reacted at 90° K with a suspension of HBr in CF_4 without violence. The layer of solid H_2O formed as the reaction product on the surface of the HBr particles prevented penetration of the ozone further into the solid particles and the reaction stopped.

OF_2 + C_2H_4. A suspension of solid ethylene in the concentrated liquid oxygen difluoride exploded violently at a temperature slightly above 77° K. However, a 10-mol % solution of OF_2 in CF_4 reacted with a 10-mol % suspension of C_2H_4 at 77° K without violence. The main reaction product was found to be CF_3OF.

ACKNOWLEDGMENT

Acknowledgment is due to all my colleagues, especially to L. V. Streng and A. V. Grosse for assistance and valuable suggestions.

RECEIVED for review September 25, 1970. Accepted February 8, 1971.