F134a Refrigerant
(recommended by John Wismer, Elf Atochem)

A major shift is occurring in the fluorochemicals industry, particularly in that part of the industry which manufactures refrigerants. This involves the shift away from chlorine containing CFC's (chlorofluorocarbons) and HCFC's (Hydrochlorofluorocarbons) to HFC's (Hydrofluorocarbons). This is because molecules containing chlorine degrade the protective ozone layer of the upper atmosphere. In automotive refrigerants, the shift has been away from R12 (Dichlorodifluoromethane) and towards R134a (1,1,1,2-tetrafluoroethane). This market is still growing as older air conditioning systems are phased out around the world. Refrigerants use a nomenclature which is universally accepted in the industry. A simplistic version involves the "rule of 90", in which 90 is added to the refrigerant's numeric code. In the resulting number, the last digit denotes the number of fluorine atoms, the second to the last, the number of hydrogen atoms, and the third from the last, the number of carbon atoms. When another digit occurs, it denotes the number of chlorine atoms. When the compound is unsaturated, an extra digit is added to the left to indicate the degree of saturation; "1" indicates a double bond in the molecule. The suffix letters denote the isomers based on symmetry considerations.

A major focus of the fluorochemicals industry has been to make use of retired HCFC or CFC manufacturing equipment in the manufacture of new refrigerants. This project involves Penn Refrigerants, a company with a fluorochemicals complex, which has several pieces of unused equipment, particularly for distillation. It has a significant infrastructure for handling emissions, including an aqueous acid neutralization system, an incinerator for liquid organic wastes containing acids, and a thermal oxidizer for combustion of gaseous wastes. In other words, small waste streams should not be a problem. It also has significant utilities infrastructure, including low temperature refrigeration (30 tons @ -40°C), a boiler plant capable of producing 150 psig steam with 20K lb/hr of unused capacity, an electrical substation which can supply both 460V and 220V 3-phase power, and a large excess of cooling tower capacity.

Penn Refrigerants is aware that there are several technologies available to manufacture F134a. They are considering licensing ICI's patented process. You (Quaker Consultants) have been approached to evaluate the capital required to retrofit the Penn Refrigerants plant on the Gulf Coast to make F134a using the ICI technology.

The ICI process is documented in U.S. Patent 5,382,722. It involves two reaction steps:

IF

$$\text{TCE} + 3\text{HF} \rightarrow \text{F133a} + 2\text{HCl} \quad (1)$$

$$\text{F133a} + \text{HF} \rightarrow \text{F134a} + \text{HCl} \quad (2)$$

Not mentioned in the patent, but implied, is that gas phase reaction (2) has a relatively severe equilibrium limitation. Its heat of reaction is about 6.5 kcal/mol (i.e., endothermic) and the entropy of reaction is about -2.5 cal/mol-K. Also, the patent mentions a R1122 impurity which boils in the same range as F134a. This is the most troublesome olefin, but there may be others. One way to destroy these olefins is with chlorination technology. Penn Refrigerants has chlorine storage and feed systems available in their plant. Chlorination can be accomplished photochemically or perhaps, more simply, catalytically. The R134a molecule is resistant to chlorination at the temperatures used to saturate the double bond. The saturated chlorine-containing compound is much less volatile than F134a.

Penn Refrigerants has placed constraints on its plant:

Gaseous HF or HCl cannot be compressed.

HCl must be recovered by distillation and absorbed into aqueous form at 36% concentration.

Inconel 600 or better is required for reactor and HF reboiler service

There are useful VLE data for mixtures of HF, F133a, and F134a in the *Journal of Fluorine Chemistry,* **61**, 123-131 (1993). Some LLE data are in European Patent No. 0 509 449 A2. Hydrogen fluoride has some odd thermodynamic characteristics which can make equipment design of HF systems tricky. A good guess at its enthalpy chart with a good discussion appears in a paper by Yarboff and Lightcap (*J. Chem. Eng. Data,* **9**, 2, 178, 1964). ASPEN PLUS uses a special equation of state to approximate the HF association effects. Does this approximation agree with the Yarboff and Lightcap chart? If not, how might this affect your design?

A listing of major equipment is as follows:

Off Sites

- Rail Car Unloading Station with ½ mi spur
- Aqueous HCl Storage
- Boiler Plant (20K lb/hr excess cap)
- Refrigeration at -40°C (30 ton)
- Cooling Towers - much excess capacity
- Waste Water Lagoon and Neutralization
- Liquid Waste Incinerator
- Thermal Oxidizer (Gaseous Waste)
- High Pressure Refrigerant Storage (400 psig) – 4 x 20,000 gal
- HF Storage - 4 x 20,000 gal
- Organic Feed Storage - 200,000 gal
- Chlorine Storage – 5,000 gal

Process Equipment:

- 3 3 ft x 80 ft Distillation Cols. with Pall ring random packing (304SS)
- 3 Condenser Systems – 3,000 ft^2, 1,000 ft^2, 600 ft^2; CS Shell/SS Tubes
- 3 Reboiler Systems - all 150 ft^2; CS Shell/SS Tubes
- HF Feed Station (1 pump with in line spare; day tank)
- Organic Feed Station (1 pump with in line spare, day tank)
- Chlorine Feed Station (1 pump with in line spare)
- Chlorine Vaporizer (100 ft^2)
- Aqueous HCl Storage - 300K gal

References:

U.S. Patent 5,382,722.

Journal of Fluorine Chemistry, **61**, 123-131 (1993).

European Patent No. 0 509 449 A2.

Yarboff and Lightcap, *J. Chem. Eng. Data,* **9**, 2, 178 (1964).