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ABSTRACT

The basic physical properties and thermodynamic constants of aluminum chloride have been calculated to obtain the data required for engineering calculations of thermodynamic cycles employing aluminum chloride vapor. The possible corrosion problems involved were evaluated from the standpoint of basic chemical thermodynamics, and it was concluded that high-nickel-content alloys would contain aluminum chloride satisfactorily.

The advantages of gaseous aluminum chloride as an intermediate heat transfer medium in a molten-salt-fueled reactor were evaluated. It was determined that the temperature range of the molten-salt heat transfer system was too low to utilize aluminum chloride effectively. A gas-turbine cycle employing aluminum chloride as the working fluid and a binary vapor cycle employing water vapor for the lower temperature cycle were also considered. Neither of these studies showed aluminum chloride to have outstanding advantages. It is believed, however, that special applications may be found in which it will be possible to exploit the unique characteristics of aluminum chloride.

INTRODUCTION

Gaseous aluminum chloride appears to be attractive as a heat transfer medium and as a thermodynamic-cycle working fluid as a consequence of the fact that it exists as the monomer $AlCl_3$ at high temperatures and as the dimer Al_2Cl_6 at low temperatures. The effective specific heat and thermal conductivity of a gas that associates are considerably enhanced because of the association equilibrium at temperatures at which there is an appreciable fraction of both monomer and polymer, and therefore aluminum chloride may be an exceptionally good heat transfer medium for some applications. Its possibilities as the working fluid in a thermodynamic cycle stem from the fact that, in an idealized gas turbine with a negligible pressure drop in the system, the pump compressor will require work proportional to the compressor inlet temperature times the specific gas constant of the dimer for any given pressure ratio. In the high-temperature region at the turbine, on the other hand, if the gas is completely monomeric, this same weight of gas will do work proportional to the turbine inlet temperature times the monomer gas constant for the same pressure ratio. Because of the relatively large difference in the gas constant between the monomer and dimer, the ratio of turbine work to compressor work will be greater than for a gas that does not dissociate. Further, the energy losses due to the inefficiency of both the compressor and the turbine will have relatively smaller effects on the over-all thermal efficiency with a dissociating gas as the working fluid.

BASIC PHYSICAL PROPERTIES OF ALUMINUM CHLORIDE

The objective of this study was to investigate the possible advantages of aluminum chloride arising from its dissociation and the consequent increase in effective specific heat and thermal conductivity. Qualitatively the reason for these increases is simple. Lowering the temperature of the gas will yield not only the heat given off if the composition of the gas were "frozen," but, since the gas is more highly associated at lower temperatures, it will also give off the chemical heat due to the association of some of the monomer molecules as a result of lowering the temperature. The same phenomenon increases the thermal conductivity. The thermal conductivity is the amount of heat that would be transferred in unit time across unit area from a temperature $T + dT$ to T divided by the temperature gradient, dT/dx. The frozen thermal conductivity is that which would occur if the composition were frozen at an average weight fraction $\bar{w}_n$ of the polymer and $\bar{w}_1$ of the monomer at both temperatures. Since w_1 is higher at $T + dT$ and w_n is higher at T than the average, relatively more monomer would diffuse from $T + dT$ to T and more polymer from T to $T + dT$ than for a frozen composition. The composition of the higher-temperature gas molecules diffusing to the lower temperature would change with a trend toward the lower equilibrium concentration of monomer at the lower temperature and would give off heat in the process. This chemical heat contribution is part of the heat flux.

Quantitative expressions for these phenomena have been given by Butler and Brokaw.[1] For a substance which dimerizes,

$$C_{pe} = C_{pf} + \frac{\Delta H^2}{RT^2}\,\frac{w_1 w_2 (1 + w_1)}{4M_1}\,, \qquad (1)$$

$$\lambda_e = \lambda_f + \frac{\Delta H^2}{RT^2}\left(\frac{D_{12}P}{R'T}\right)\left(\frac{w_1 w_2}{2}\right), \qquad (2)$$

where

C_{pe} = effective specific heat in $\mathrm{cal \cdot g^{-1} \cdot deg^{-1}}$,
C_{pf} = frozen specific heat,
ΔH = heat change for the reaction $Al_2Cl_6 \rightleftharpoons 2AlCl_3$,
R, R' = gas constants in proper units,
w_1, w_2 = weight fraction of monomer and dimer, respectively,
λ_e = effective thermal conductivity in $\mathrm{cal \cdot cm^{-1} \cdot sec^{-1} \cdot deg^{-1}}$,
λ_f = frozen thermal conductivity,
D_{12} = interdiffusion coefficients of monomer and dimer,
P = total pressure,
M_1 = molecular weight of a monomer.

The quantities of practical interest, the effective specific heat, C_{pe}, the effective thermal conductivity, λ_e, and the viscosity, have never been measured. These and other quantities of interest must be estimated. It is fortunate that the theory of gases is well developed and, for some calculations, is more reliable than measurements.

Effective Specific Heat

The effective specific heat was calculated by use of Eq. (1). The frozen specific heat of Al_2Cl_6, C_{pf}, was estimated according to well-known statistical mechanical methods[2] by use of the infrared vibrational frequencies measured or estimated by Klemperer.[3] The frequencies for $AlCl_3$ were estimated by analogy with the compound BCl_3 (ref 4). The average value of the specific heat in the temperature range 500 to 1000°K is 0.16 $\mathrm{cal \cdot g^{-1} \cdot (^\circ C)^{-1}}$ for Al_2Cl_6 and is 0.14 $\mathrm{cal \cdot g^{-1} \cdot (^\circ C)^{-1}}$ for $AlCl_3$. At each composition of the gas, an average value was computed from the composition-weighted average of these two values for the monomer and the dimer.

The composition of the gas may be computed from the equilibrium constant

$$K = \frac{P_1^2}{P_2} = \frac{4w_1^2}{1 - w_1^2}\,P\,, \qquad (3a)$$

where

$$\Delta F^\circ = \Delta H - T\Delta S^\circ = -RT \ln K\,, \qquad (3b)$$

in which ΔH is the heat of dissociation of the gas, which was taken as 29.6 kcal/mole (ref 5), and ΔS° is the entropy difference between 2 moles of $AlCl_3$ at 1 atm pressure and 1 mole of Al_2Cl_6 at 1 atm pressure, which was taken as 34.6 $\mathrm{cal \cdot mole^{-1} \cdot deg^{-1}}$ (ref 5). The values of w_1 calculated from Eqs. (3*a*) and (3*b*) at pressures of 0.1, 1, and 10 atm, respectively, in the temperature range 500 to 1200°K are listed in column 2 of Table 1. Column 3 of the same table lists the

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[1] J. N. Butler and R. S. Brokaw, *J. Chem. Phys.* **26**, 1636 (1957).

[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, New York, 1940.

[3] W. Klemperer, *J. Chem. Phys.* **24**, 353 (1956).

[4] G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, New York, 1945.

[5] A. Shepp and S. H. Bauer, *J. Am. Chem. Soc.* **76**, 265 (1954).

Table 1. Calculated Values of w_1, C_{pe}, $\overline{\lambda}_f$, and λ_e for Aluminum Chloride

Temperature ($^{\circ}$K)	Weight Fraction of Monomer, w_1	C_{pe} ($cal \cdot g^{-1} \cdot deg^{-1}$)	$\overline{\lambda}_f$ ($cal \cdot cm^{-1} \cdot sec^{-1} \cdot deg^{-1}$)	λ_e ($cal \cdot cm^{-1} \cdot sec^{-1} \cdot deg^{-1}$)
		For a Pressure of 0.1 atm		
			$\times 10^{-6}$	$\times 10^{-6}$
500	0.003	0.17	12	14
550	0.013	0.19	13	18
600	0.038	0.25	13	26
650	0.100	0.35	14	42
700	0.223	0.51	15	63
750	0.422	0.66	16	77
800	0.655	0.63	17	68
850	0.831	0.43	18	47
900	0.926	0.28	19	32
950	0.966	0.20	19	25
1000	0.984	0.17	20	23
1050	0.992	0.15	20+	22
1100	0.996	0.15	21	22
1150	0.998	0.14	21	21+
1200	0.999	0.14	22	22–
		For a Pressure of 1 atm		
			$\times 10^{-6}$	$\times 10^{-6}$
500	0.001	0.16	12	13
550	0.004	0.17	13	15
600	0.012	0.19	13	17
650	0.032	0.22	14	24
700	0.072	0.28	15	34
750	0.145	0.36	15	46
800	0.264	0.47	16	60
850	0.428	0.55	17	68
900	0.612	0.54	18	63
950	0.766	0.44	19	50
1000	0.870	0.32	19	37
1050	0.929	0.24	20	30
1100	0.961	0.19	20	25
1150	0.978	0.17	21	24
1200	0.987	0.16	22	24

Table 1 (continued)

Temperature (°K)	Weight Fraction of Monomer, w_1	C_{pe} (cal·g^{-1}·deg^{-1})	$\bar{\lambda}_f$ (cal·cm^{-1}·sec^{-1}·deg^{-1})	λ_e (cal·cm^{-1}·sec^{-1}·deg^{-1})
		For a Pressure of 10 atm		
			$\times 10^{-6}$	$\times 10^{-6}$
500	0.000	0.16	12	12
550	0.001	0.16	13	14
600	0.004	0.17	13	14
650	0.010	0.18	14	17
700	0.023	0.20	14	20
750	0.047	0.23	15	26
800	0.087	0.27	16	34
850	0.148	0.32	16	42
900	0.240	0.38	17	52
950	0.352	0.43	18	58
1000	0.490	0.46	18	59
1050	0.622	0.44	19	54
1100	0.740	0.38	20	47
1150	0.827	0.30	21	40
1200	0.888	0.25	21	33

values of C_{pe} estimated by use of Eq. (1) for the three pressures and the same temperature range. A plot of C_{pe} and the average frozen specific heat $\bar{C}_{pf}$ vs temperature at the three pressures is presented in Fig. 1.

Effective Thermal Conductivities

The effective thermal conductivities were calculated using Eq. (2). The frozen thermal conductivities of monomer and of dimer were calculated from the equation[6]

$$\lambda_f = \frac{(1.9891 \times 10^{-4})(T/M_n)^{1/2}}{\sigma_n^2 \Omega} \left(\frac{4}{15}\frac{C_v}{R} + \frac{3}{5}\right) , \quad (4)$$

where M_n is the molecular weight of a polymer, σ_n is the average effective molecular diameter of a polymer in angstroms, and Ω is a factor which corrects for intermolecular interactions and can be calculated theoretically for simple potential functions in terms of the parameters of the potential function.[7]

A crude estimate of σ_n^2 was made for Al_2Cl_6 and $AlCl_3$. From electron diffraction data on Al_2Cl_6 (ref 8), structural estimates for $AlCl_3$ (ref 5), and the van der Waals radii of chlorine atoms, the dimensions of Al_2Cl_6 and $AlCl_3$ were estimated. By comparison of the relative dimensions of similar compounds to their effective collision diameters,[9] the effective collision diameters of Al_2Cl_6 and $AlCl_3$ were estimated. For the

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[6] J. O. Hirschfelder, C. F. Curtiss, and R. B. Byrd, *Molecular Theory of Gases and Liquids*, pp 14, 528, 534, Wiley, New York, 1954.

[7] For a more accurate equation see J. O. Hirschfelder, *J. Chem. Phys.* 26, 282 (1957). The use of the more accurate equation leads to only a relatively small difference from the values calculated here.

[8] L. R. Maxwell, *J. Opt. Soc. Am.* 30, 374 (1940).

[9] Hirschfelder, Curtiss, and Byrd, *op. cit.*, Table I-A, pp 1111–12, 162.

Lennard-Jones 6-12 interaction potential, Ω has been calculated as a function of the parameter kT/ϵ, where ϵ is the depth of the potential well. The value of ϵ is unknown for either Al_2Cl_6 or $AlCl_3$. We may, however, estimate ϵ by analogy with other halogen-containing compounds. Of several halogen-containing compounds[9] the lowest value of ϵ/k is 324 for HI and the highest is 1550 for $SnCl_4$. With these values as limits, the following values were obtained for Ω:

T (°K)	ϵ/k	Ω
500	324	1.3
	1550	2.7
1000	324	1.0
	1550	2.0

The range of values of Ω listed is 1.0 to 2.7, and a value of $\Omega = 2$ was arbitrarily chosen as being reasonable. The value of $D_{12}P$ was estimated from the equation[10]

$$D_{12}P = \frac{0.0026280}{\sigma_{12}^2 \Omega'} \left(T^3 \frac{M_1 + M_2}{2M_1M_2} \right)^{1/2} , \quad (5)$$

where M_1 and M_2 are the molecular weights of monomer and dimer, respectively, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, and Ω' is a correction for intermolecular interactions. It does not differ greatly from Ω, and therefore the value 2.0 was used. The calculated values of $D_{12}P$ in the temperature range 500 to 1200°K are listed in column 2 of Table 2. The average frozen thermal conductivities, $\overline{\lambda}_f$, and the effective thermal conductivity, λ_e, calculated from Eq. (2), at pressures of 0.1, 1, and 10 atm were listed in Table 1. Plots of $\overline{\lambda}_f$ and λ_e vs temperature at the three pressures are presented in Fig. 2.

The constants and parameters used in these calculations are summarized below:

$R = 1.9869$ cal·mole^{-1}·deg^{-1}

$R' = 82.057$ cm^3·atm·mole^{-1}·deg^{-1}

$\Delta H = 29.6$ kcal for the reaction
$Al_2Cl_6 \rightleftharpoons 2AlCl_3$

$\Delta S^\circ = 34.6$ e.u., entropy change for reaction $Al_2Cl_6 \rightleftharpoons 2AlCl_3$ with both monomer and dimer at their standard state of 1 atm

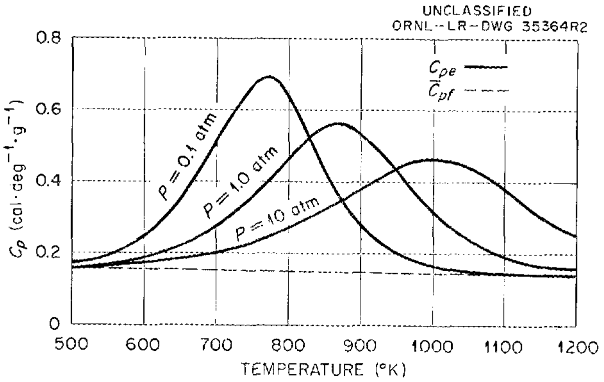

Fig. 1. The Calculated Effective Specific Heat of Aluminum Chloride as a Function of Temperature at Three Pressures.

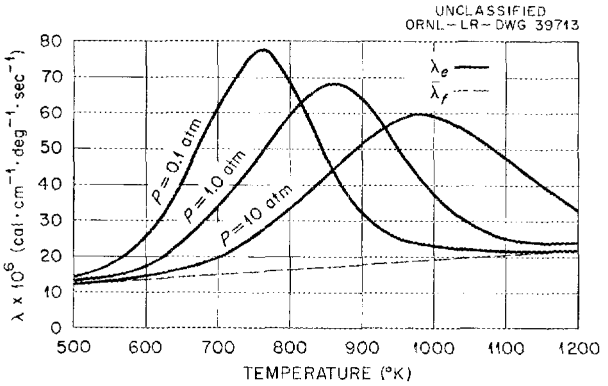

Fig. 2. The Calculated Effective Thermal Conductivities of Aluminum Chloride as a Function of Temperature at Three Pressures.

$\sigma_1^2 = 40$ Å^2

$\sigma_2^2 = 65$ Å^2

$\sigma_{12}^2 = 51.7$ Å^2

$M_1 = M_2/2 = 133.35$ g/mole

$\Omega = \Omega' = 2.0$

$C_v = C_p - R$

Viscosity

The viscosity was estimated from the equation[6]

$$\eta_n = \frac{2.6693 \times 10^{-5} (M_n T)^{1/2}}{\sigma_n^2 \Omega} \quad (6)$$

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[10] *Ibid.*, p 539.

Table 2. Values of $D_{12}P$, η_1, and η_2

T (°K)	$D_{12}P$ ($cm^2 \cdot atm \cdot sec^{-1}$)	Viscosity of Monomer, η_1 ($g \cdot cm^{-1} \cdot sec^{-1}$)	Viscosity of Dimer, η_2 ($g \cdot cm^{-1} \cdot sec^{-1}$)
	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-6}$
500	21.3	86	75
550	24.6	90	79
600	28.0	94	82
650	31.6	98	86
700	35.3	102	89
750	39.2	106	92
800	43.1	109	95
850	47.2	112	98
900	51.5	116	101
950	55.8	119	103
1000	60.3	122	106
1050	64.8	125	109
1100	69.6	128	111
1150	74.3	131	114
1200	79.2	134	116

for both monomer and dimer. The calculated values are listed in columns 3 and 4 of Table 2. For a mixture of monomer and dimer, a composition weighted average would be an adequate approximation to the viscosity.

Vapor Pressure

The vapor pressure of solid aluminum chloride in equilibrium with the gaseous phase may be calculated from the equation[11]

$$\log P \text{ (atm)} = \frac{-6360}{T} + 3.77 \log T - 0.00612T + 6.78 \ . \qquad (7)$$

The vapor pressure is 1 atm at 180°C (453°K).

Velocity of Sound in Aluminum Chloride

The velocity of sound, C_0, in the working fluid is needed for turbine design. At frequencies low enough so that the velocity of association and dissociation of the aluminum chloride is fast enough to follow the compression and rarefaction of the gas, the velocity of sound may be calculated from[6]

$$C_0^2 = \frac{-v^2}{(\partial v/\partial P)_S} \ , \qquad (8)$$

where C_0 is the velocity of sound in cm/sec, v is the specific volume of the gas in cm^3/g, P is the pressure in $dynes/cm^2$, and S is the entropy. The value of $(\partial v/\partial P)_S$ can be calculated from the exact thermodynamic relation[12]

$$\left(\frac{\partial v}{\partial P}\right)_S = \left(\frac{\partial v}{\partial P}\right)_T + \frac{T}{C_{pe}}\left(\frac{\partial v}{\partial T}\right)_P^2 \qquad (9)$$

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[11] O. Kubaschewski and E. L. Evans, *Metallurgical Thermochemistry*, Wiley, New York, 1956.

[12] G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical substances*, p 164, McGraw-Hill, New York, 1923.

and the equation

$$Pv = \left(\frac{1 + w_1}{M_2}\right) RT \ , \tag{10}$$

in which the reasonable assumption is made that the gaseous monomer and dimer individually behave as ideal gases and that all deviations from an ideal gas are due to the association or dissociation of the gaseous monomer or dimer. An evaluation of $(\partial v/\partial P)_T$ and $(\partial v/\partial T)_P$ from Eq. (10) and the thermodynamic relation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} = \frac{d \ln [4w_1^2 P/(1 - w_1^2)]}{dT} \tag{11}$$

leads to

$$\left(\frac{\partial v}{\partial P}\right)_T = -\frac{v}{P}\left(1 + \frac{w_1 w_2}{2}\right)$$

$$= -\frac{RT}{P^2}\left(\frac{1 + w_1}{M_2}\right)\left(1 + \frac{w_1 w_2}{2}\right) \tag{12}$$

and

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{v}{T}\left(1 + \frac{\Delta H}{RT}\frac{w_1 w_2}{2}\right)$$

$$= \frac{R}{P}\left(\frac{1 + w_1}{M_2}\right)\left(1 + \frac{\Delta H}{RT}\frac{w_1 w_2}{2}\right) \ . \tag{13}$$

Substitution of Eqs. (12) and (13) into Eq. (9) leads to

$$\left(\frac{\partial v}{\partial P}\right)_s = -\frac{RT}{P^2}\left(\frac{1 + w_1}{M_2}\right)\left[1 + \frac{w_1 w_2}{2} - \frac{R(1 + w_1)}{M_2 C_{pe}}\left(1 + \frac{\Delta H}{RT}\frac{w_1 w_2}{2}\right)^2\right] \ . \tag{14}$$

THERMODYNAMIC PROPERTIES

In the gaseous phase the state of an equilibrium mixture of Al_2Cl_6 and $AlCl_3$ is determined by any two independent properties, and knowledge of the thermodynamic state makes it possible to determine the thermodynamic properties. The two independent defining properties used to calculate weight fraction of monomer, enthalpy, entropy, and specific volume were temperature and pressure. The relations used in the computational procedure are summarized below.

Determination of Weight Fraction of Monomer, w_1. – It has been shown by Newton, from free-energy-change relationships, that

$$w_1 = \left(\frac{1}{2} + \frac{1}{2}\tanh u\right)^{1/2} \ , \tag{15}$$

where

$$u = 8.016 - \frac{1}{2}\ln\frac{P}{14.696} - \frac{13420}{T} \ ,$$

T is in °R, and P is pressure in psia.

Determination of Enthalpy, h. – The enthalpy of the mixture is the sum of the enthalpy the gas would have if it were all in the dimer state plus the enthalpy of dissociation. Choosing absolute zero temperature as the base for enthalpy and 0.1575 $\text{Btu}\cdot\text{lb}^{-1}\cdot(°\text{R})^{-1}$ *as the frozen specific heat* averaged for the temperatures and pressures under consideration, the "sensible" enthalpy, in Btu/lb, is

$$h_s = 0.1575T \ .$$

The enthalpy of dissociation is 199.7 Btu for each pound of Al_2Cl_6 monomerized. Therefore the total enthalpy is

$$h = 0.1575T + 199.7w_1 \ . \tag{16}$$

Determination of Entropy, s. – From the definition of entropy in $\text{Btu}\cdot\text{lb}^{-1}\cdot(°\text{R})^{-1}$,

$$ds = \frac{dQ_{\text{reversible}}}{T} \ ,$$

it can be shown[13] that

$$ds = \frac{du + P\,dv}{T} \ .$$

Noting that

$$dh = du + P\,dv + v\,dP$$

gives

$$ds = \frac{dh - v\,dP}{T} \ .$$

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[13] See, for instance, J. H. Keenan, *Thermodynamics*, p 85, Wiley, New York, 1941.

Then, for an isobaric process, that is, constant pressure,

$$\Delta s]_1^2 = \int_{T_1}^{T_2} \frac{dh}{T} \approx \frac{\Delta h}{\bar{T}} \tag{17}$$

for small variations in T, where 1 and 2 are thermodynamic states.

The entropy was considered equal to zero at 900°R and 150 psia, and the entropy at other temperatures at this pressure was approximated by a stepwise, finite-difference procedure using the approximation given above. To get the entropy at 900°R and some other pressure, it is possible to use one of Maxwell's relations[14]

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \quad .$$

For a constant temperature process, then

$$\Delta s]_1^2 = -\int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T}\right)_P dP \quad .$$

As shown below, if P is expressed in pounds per square foot (psf),

$$v = 5.793(1 + w_1)\frac{T}{P} \quad .$$

Since $(1 + w_1)$ does not vary from unity by more than about 0.3% at 900°R for the pressures under consideration, it can be stated that

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{5.793}{P} \quad ,$$

so that at constant temperature

$$\Delta s]_1^2 = -\int_{P_1}^{P_2} \frac{5.793}{P} dP$$

$$= 5.793 \ln \frac{P_1}{P_2} \qquad \text{in ft}\cdot\text{lb}\cdot\text{lb}^{-1}\cdot(^\circ\text{R})^{-1}$$

$$= 0.007444 \ln \frac{P_1}{P_2} \qquad \text{in Btu}\cdot\text{lb}^{-1}\cdot(^\circ\text{R})^{-1} \quad .$$

Determination of Specific Volume, v. – The perfect gas law states that

$$Pv = \frac{R_0}{M_m} T \quad , \tag{18}$$

where

$R_0 = 1545 \text{ ft}\cdot\text{lb}_f\cdot\text{mole}^{-1}\cdot(^\circ\text{R})^{-1}$,

and M_m is the molecular weight of the mixture and is $266.7/(1 + w_1)$. Numerically this becomes

$$v = 5.793(1 + w_1)\frac{T}{P} \qquad \text{in ft}^3/\text{lb}_m \quad ,$$

where P is expressed in psf, or

$$v = 0.04023(1 + w_1)\frac{T}{P} \qquad \text{in ft}^3/\text{lb}_m \quad ,$$

where P is in psia.

Example of Numerical Procedure. – As an example of the calculational procedure employed, a computation of weight fraction of monomer, w_1, enthalpy, h, entropy, s, and specific volume, v, at a pressure of 30 psia and a temperature of 1260°R follows:

1. For the weight fraction of monomer calculation,

$$w_1 = \left(\frac{1}{2} + \frac{1}{2}\tanh u\right)^{1/2} \quad ,$$

where

$$u = 8.016 - \frac{1}{2} \ln \frac{P}{14.696} - \frac{13420}{T}$$

$$= 8.016 - \frac{1}{2} \ln \frac{30}{14.696} - \frac{13420}{1260}$$

$$= -2.9923$$

and therefore

$$w_1 = \left[\frac{1}{2} + \frac{1}{2}\tanh(-2.9923)\right]^{1/2}$$

$$= 0.05055 \quad .$$

2. For the enthalpy calculation,

$$h = 0.1575T + 199.7w_1$$

$$= (0.1575 \times 1260) + (199.7 \times 0.05055)$$

$$= 208.53 \quad .$$

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[14] *Ibid.*, p 342.

3. For the entropy calculation, at a constant pressure,

$$\Delta s]_1^2 \approx \frac{\Delta h}{T}$$

$$\approx \frac{208.53 - 203.79}{1260}$$

$$\approx 0.003792 \ ,$$

and

$$s \approx 0.07298 \ .$$

4. For the specific volume calculation

$$v = 0.04023(1 + w_1)\frac{T}{P}$$

$$= 0.04023(1 + 0.05055)\frac{1260}{30}$$

$$= 1.7751 \ .$$

Data obtained for these functions at temperatures from 900 to 2000°R and pressures of 1.5, 5, 15, 30, 60, 100, and 150 psia are listed in Table 3, and an enthalpy-entropy chart is presented in Fig. 3.

CORROSION BEHAVIOR

The corrosiveness of the gas is another important consideration. The free energies of formation of aluminum chloride and the chlorides of some possible container materials at 500 and 1000°K

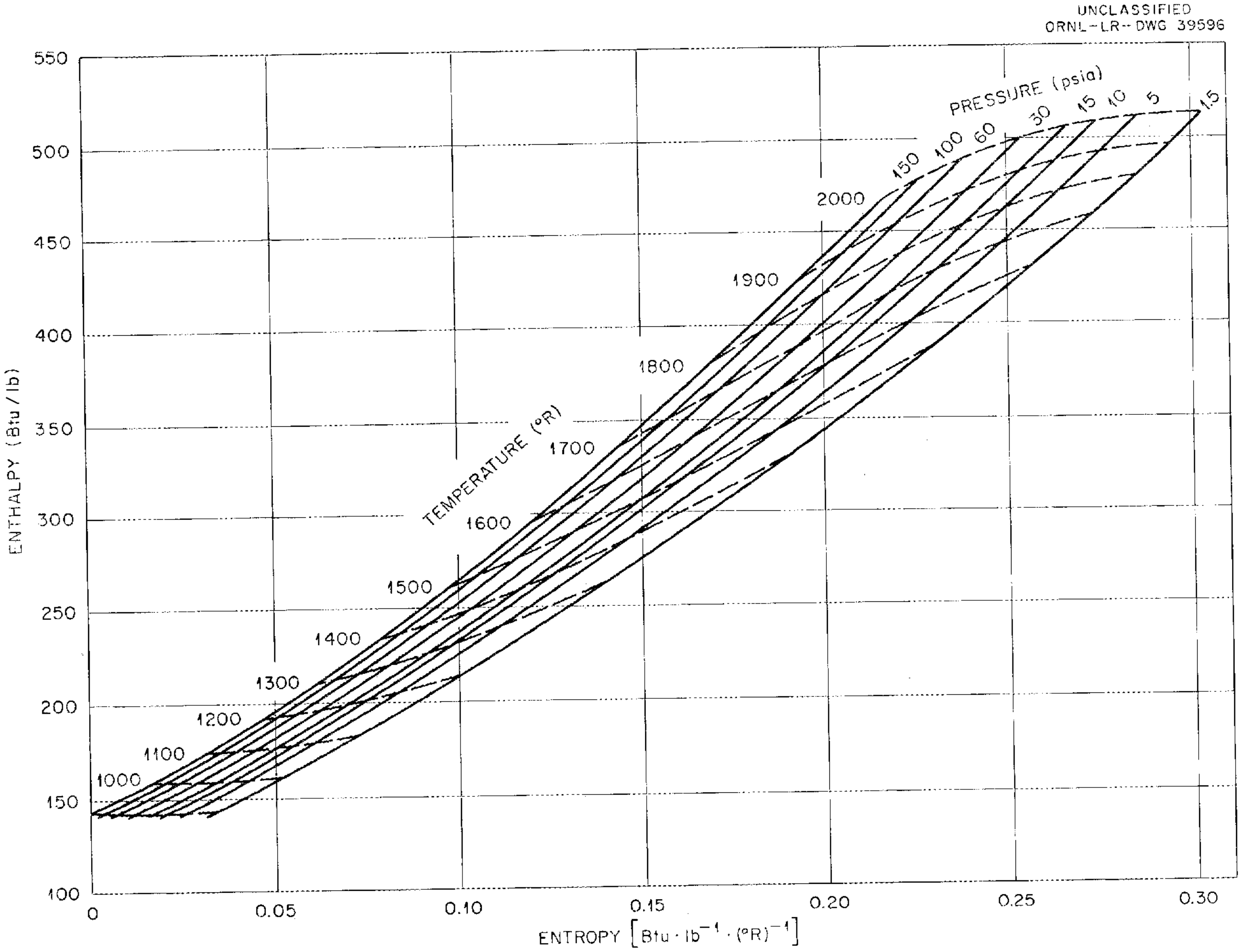

Fig. 3. Enthalpy-Entropy Diagram for Aluminum Chloride Vapor.

Table 3. Thermodynamic Data for Aluminum Chloride at Various Pressures

Temperature (°R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy [Btu·lb^{-1}·(°R)$^{-1}$]	Specific Volume (ft^3/lb)
At a Pressure of 1.5 psia				
900	0.00321	142.39	0.03425	24.193
920	0.00442	145.78	0.03794	24.761
940	0.00605	149.25	0.04164	25.340
960	0.00811	152.81	0.04535	25.932
980	0.01083	156.51	0.04911	26.544
1000	0.01422	160.33	0.05294	27.176
1020	0.01848	164.33	0.05686	27.836
1040	0.02382	168.55	0.06092	28.531
1060	0.03037	173.00	0.06512	29.266
1080	0.03836	177.75	0.06951	30.049
1100	0.04808	182.84	0.07414	30.892
1120	0.05973	188.31	0.07903	31.803
1140	0.07361	194.23	0.08422	32.795
1160	0.09006	200.66	0.08976	33.882
1180	0.10933	207.66	0.09569	35.076
1200	0.13176	215.28	0.10204	36.391
1220	0.15765	223.60	0.10886	37.844
1240	0.18725	232.65	0.11616	39.448
1260	0.22072	242.48	0.12396	41.214
1280	0.25820	253.11	0.13226	43.154
1300	0.29959	264.51	0.14104	45.270
1320	0.34464	276.65	0.15023	47.560
1340	0.39288	289.42	0.15977	50.013
1360	0.44360	302.70	0.16952	52.608
1380	0.49587	316.27	0.17936	55.314
1400	0.54854	329.93	0.18912	58.091
1420	0.60041	343.43	0.19862	60.895
1440	0.65030	356.53	0.20772	63.678
1460	0.69718	369.03	0.21629	66.396
1480	0.74025	380.78	0.22422	69.014
1500	0.77900	391.66	0.23148	71.504
1520	0.81324	401.64	0.23804	73.852
1540	0.84299	410.72	0.24394	76.052
1560	0.86851	418.96	0.24922	78.106
1580	0.89016	426.43	0.25395	80.024
1600	0.90837	433.22	0.25819	81.818
1620	0.92359	439.40	0.26201	83.501
1640	0.93625	445.08	0.26547	85.088
1660	0.94676	450.32	0.26863	86.593
1680	0.95546	455.21	0.27154	88.028
1700	0.96267	459.80	0.27424	89.405
1720	0.96863	464.14	0.27676	90.731
1740	0.97358	468.27	0.27914	92.017
1760	0.97768	472.24	0.28139	93.268
1780	0.98109	476.07	0.28355	94.491

Table 3 (continued)

Temperature (°R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy $[Btu \cdot lb^{-1} \cdot (°R)^{-1}]$	Specific Volume (ft^3/lb)
At a Pressure of 1.5 psia				
1800	0.98394	479.79	0.28561	95.690
1820	0.98631	483.42	0.28760	96.869
1840	0.98830	486.96	0.28953	98.031
1860	0.98997	490.45	0.29140	99.180
1880	0.99138	493.88	0.29323	100.31
1900	0.99257	497.26	0.29501	101.44
1920	0.99357	500.61	0.29675	102.56
1940	0.99443	503.93	0.29847	103.67
1960	0.99516	507.23	0.30015	104.78
1980	0.99578	510.50	0.30180	105.88
2000	0.99631	513.76	0.30343	106.98
At a Pressure of 5 psia				
900	0.00176	142.10	0.02530	7.2476
920	0.00242	145.38	0.02886	7.4135
940	0.00331	148.71	0.03241	7.5814
960	0.00444	152.08	0.03592	7.7515
980	0.00593	155.53	0.03944	7.9247
1000	0.00777	159.05	0.04296	8.1012
1020	0.01012	162.67	0.04650	8.2825
1040	0.01305	166.40	0.05010	8.4694
1060	0.01662	170.26	0.05374	8.6627
1080	0.02102	174.29	0.05747	8.8643
1100	0.02636	178.50	0.06130	9.0757
1120	0.03274	182.93	0.06525	9.2981
1140	0.04039	187.60	0.06935	9.5343
1160	0.04947	192.57	0.07363	9.7862
1180	0.06013	197.84	0.07810	10.056
1200	0.07260	203.48	0.08280	10.346
1220	0.08712	209.53	0.08776	10.661
1240	0.10384	216.01	0.09299	11.003
1260	0.12300	222.99	0.09852	11.374
1280	0.14484	230.49	0.10438	11.779
1300	0.16951	238.56	0.11059	12.221
1320	0.19714	247.23	0.11715	12.703
1340	0.22784	256.50	0.12408	13.226
1360	0.26166	266.40	0.13135	13.793
1380	0.29850	276.90	0.13896	14.404
1400	0.33816	287.96	0.14686	15.060
1420	0.38032	299.52	0.15500	15.756
1440	0.42452	311.49	0.16332	16.489
1460	0.47013	323.74	0.17171	17.254
1480	0.51642	336.12	0.18007	18.041
1500	0.56258	348.48	0.18831	18.841
1520	0.60782	360.66	0.19632	19.645

Table 3 (continued)

Temperature (°R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy $[Btu \cdot lb^{-1} \cdot (°R)^{-1}]$	Specific Volume (ft^3/lb)
		At a Pressure of 5 psia		
1540	0.65132	372.48	0.20400	20.442
1560	0.69243	383.84	0.21128	21.223
1580	0.73062	394.60	0.21810	21.981
1600	0.76553	404.72	0.22442	22.708
1620	0.79699	414.15	0.23024	23.401
1640	0.82497	422.88	0.23556	24.059
1660	0.84960	430.94	0.24042	24.681
1680	0.87106	438.37	0.24484	25.268
1700	0.88963	445.23	0.24887	25.823
1720	0.90560	451.56	0.25256	26.348
1740	0.91926	457.44	0.25593	26.845
1760	0.93093	462.92	0.25905	27.319
1780	0.94085	468.05	0.26193	27.771
1800	0.94929	472.88	0.26461	28.205
1820	0.95645	477.46	0.26713	28.624
1840	0.96254	481.82	0.26950	29.028
1860	0.96771	486.01	0.27175	29.421
1880	0.97211	490.03	0.27389	29.804
1900	0.97586	493.93	0.27594	30.178
1920	0.97906	497.72	0.27792	30.545
1940	0.98179	501.41	0.27982	30.906
1960	0.98413	505.03	0.28167	31.261
1980	0.98614	508.58	0.28346	31.612
2000	0.98786	512.07	0.28521	31.959
		At a Pressure of 15 psia		
900	0.00100	141.94	0.01713	2.4140
920	0.00141	145.18	0.02064	2.4686
940	0.00189	148.42	0.02409	2.5235
960	0.00256	151.71	0.02751	2.5789
980	0.00342	155.03	0.03090	2.6349
1000	0.00448	158.39	0.03426	2.6915
1020	0.00586	161.81	0.03762	2.7491
1040	0.00753	165.30	0.04097	2.8077
1060	0.00959	168.86	0.04433	2.8676
1080	0.01215	172.52	0.04772	2.9291
1100	0.01522	176.28	0.05114	2.9923
1120	0.01891	180.17	0.05461	3.0578
1140	0.02335	184.20	0.05815	3.1260
1160	0.02858	188.40	0.06176	3.1971
1180	0.03475	192.78	0.06548	3.2717
1200	0.04199	197.37	0.06931	3.3505
1220	0.05043	202.21	0.07327	3.4339
1240	0.06017	207.30	0.07738	3.5226
1260	0.07137	212.69	0.08165	3.6172

Table 3 (continued)

Temperature (^{o}R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy [$Btu \cdot lb^{-1} \cdot (^{o}R)^{-1}$]	Specific Volume (ft^3/lb)
		At a Pressure of 15 psia		
1280	0.08421	218.40	0.08611	3.7186
1300	0.09882	224.46	0.09078	3.8276
1320	0.11532	230.90	0.09566	3.9449
1340	0.13388	237.75	0.10077	4.0713
1360	0.15464	245.05	0.10613	4.2077
1380	0.17770	252.80	0.11175	4.3549
1400	0.20313	261.02	0.11762	4.5134
1420	0.23099	269.73	0.12375	4.6839
1440	0.26129	278.92	0.13014	4.8668
1460	0.29395	288.59	0.13676	5.0621
1480	0.32881	298.69	0.14359	5.2697
1500	0.36567	309.20	0.15059	5.4891
1520	0.40421	320.04	0.15772	5.7192
1540	0.44404	331.13	0.16492	5.9588
1560	0.48467	342.39	0.17214	6.2061
1580	0.52559	353.70	0.17930	6.4589
1600	0.56622	364.96	0.18634	6.7148
1620	0.60601	376.04	0.19318	6.9715
1640	0.64443	386.86	0.19977	7.2264
1660	0.68101	397.31	0.20607	7.4773
1680	0.71540	407.32	0.21203	7.7222
1700	0.74732	416.84	0.21763	7.9595
1720	0.77661	425.83	0.22285	8.1881
1740	0.80320	434.28	0.22771	8.4073
1760	0.82712	442.21	0.23222	8.6168
1780	0.84848	449.62	0.23638	8.8166
1800	0.86741	456.54	0.24023	9.0069
1820	0.88410	463.02	0.24379	9.1884
1840	0.89874	469.10	0.24709	9.3616
1860	0.91154	474.80	0.25015	9.5271
1880	0.92270	480.18	0.25301	9.6858
1900	0.93242	485.26	0.25569	9.8383
1920	0.94085	490.10	0.25821	9.9852
1940	0.94818	494.71	0.26059	10.127
1960	0.95454	499.13	0.26284	10.265
1980	0.96006	503.38	0.26499	10.399
2000	0.96486	507.49	0.26704	10.529
		At a Pressure of 30 psia		
900	0.00072	141.89	0.01197	1.2066
920	0.00097	145.09	0.01545	1.2338
940	0.00136	148.32	0.01888	1.2611
960	0.00179	151.55	0.02225	1.2885
980	0.00241	154.83	0.02559	1.3161
1000	0.00318	158.13	0.02889	1.3440

Table 3 (continued)

Temperature (°R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy $[Btu \cdot lb^{-1} \cdot (°R)^{-1}]$	Specific Volume (ft^3/lb)
At a Pressure of 30 psia				
1020	0.00412	161.47	0.03217	1.3722
1040	0.00534	164.86	0.03543	1.4008
1060	0.00680	168.30	0.03867	1.4298
1080	0.00857	171.81	0.04192	1.4593
1100	0.01075	175.39	0.04518	1.4896
1120	0.01338	179.07	0.04846	1.5206
1140	0.01649	182.83	0.05177	1.5525
1160	0.02020	186.73	0.05512	1.5855
1180	0.02459	190.75	0.05853	1.6198
1200	0.02971	194.92	0.06201	1.6555
1220	0.03566	199.26	0.06556	1.6928
1240	0.04258	203.79	0.06922	1.7320
1260	0.05055	208.53	0.07298	1.7734
1280	0.05965	213.50	0.07686	1.8172
1300	0.07003	218.72	0.08087	1.8637
1320	0.08181	224.22	0.08504	1.9132
1340	0.09510	230.02	0.08937	1.9660
1360	0.11001	236.14	0.09387	2.0225
1380	0.12664	242.61	0.09856	2.0830
1400	0.14513	249.45	0.10345	2.1479
1420	0.16558	256.68	0.10854	2.2175
1440	0.18800	264.30	0.11383	2.2920
1460	0.21249	272.34	0.11933	2.3717
1480	0.23905	280.79	0.12504	2.4568
1500	0.26767	289.65	0.13095	2.5476
1520	0.29827	298.90	0.13704	2.6439
1540	0.33071	308.52	0.14328	2.7456
1560	0.36481	318.48	0.14967	2.8525
1580	0.40031	328.71	0.15614	2.9642
1600	0.43692	339.16	0.16268	3.0802
1620	0.47426	349.76	0.16922	3.1998
1640	0.51192	360.42	0.17572	3.3220
1660	0.54945	371.06	0.18213	3.4460
1680	0.58643	381.59	0.18839	3.5708
1700	0.62244	391.92	0.19447	3.6953
1720	0.65708	401.98	0.20032	3.8186
1740	0.69004	411.71	0.20591	3.9398
1760	0.72105	421.05	0.21122	4.0582
1780	0.74994	429.96	0.21622	4.1732
1800	0.77659	438.42	0.22093	4.2844
1820	0.80097	446.44	0.22533	4.3915
1840	0.82310	454.00	0.22944	4.4943
1860	0.84305	461.14	0.23328	4.5929
1880	0.86095	467.85	0.23685	4.6873
1900	0.87691	474.19	0.24018	4.7778

Table 3 (continued)

Temperature ($^{\circ}$R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy $[\mathrm{Btu \cdot lb^{-1} \cdot (^{\circ}R)^{-1}}]$	Specific Volume (ft^3/lb)
At a Pressure of 30 psia				
1920	0.89110	480.17	0.24330	4.8646
1940	0.90367	485.83	0.24622	4.9479
1960	0.91477	491.19	0.24895	5.0281
1980	0.92456	496.30	0.25153	5.1054
2000	0.93318	501.17	0.25397	5.1801
At a Pressure of 60 psia				
900	0.00049	141.84	0.00681	0.60320
920	0.00071	145.04	0.01028	0.61674
940	0.00093	148.23	0.01368	0.63029
960	0.00130	151.46	0.01704	0.64393
980	0.00171	154.69	0.02034	0.65762
1000	0.00223	157.94	0.02359	0.67139
1020	0.00293	161.23	0.02682	0.68529
1040	0.00374	164.54	0.03000	0.69929
1060	0.00479	167.90	0.03317	0.71349
1080	0.00608	171.31	0.03632	0.72788
1100	0.00759	174.76	0.03946	0.74247
1120	0.00945	178.28	0.04261	0.75737
1140	0.01168	181.88	0.04576	0.77260
1160	0.01430	185.55	0.04892	0.78818
1180	0.01737	189.31	0.05211	0.80420
1200	0.02100	193.19	0.05534	0.82075
1220	0.02524	197.18	0.05862	0.83790
1240	0.03013	201.31	0.06194	0.85569
1260	0.03575	205.58	0.06533	0.87424
1280	0.04221	210.02	0.06880	0.89366
1300	0.04959	214.64	0.07236	0.91405
1320	0.05795	219.46	0.07601	0.93550
1340	0.06738	224.49	0.07976	0.95814
1360	0.07801	229.76	0.08364	0.98213
1380	0.08993	235.29	0.08764	1.0075
1400	0.10318	241.08	0.09178	1.0346
1420	0.11788	247.16	0.09607	1.0633
1440	0.13412	253.55	0.10050	1.0940
1460	0.15197	260.26	0.10510	1.1266
1480	0.17151	267.31	0.10986	1.1614
1500	0.19276	274.70	0.11479	1.1985
1520	0.21576	282.44	0.11988	1.2379
1540	0.24050	290.53	0.12513	1.2797
1560	0.26699	298.96	0.13054	1.3240
1580	0.29515	307.73	0.13609	1.3708
1600	0.32485	316.80	0.14176	1.4200
1620	0.35597	326.16	0.14753	1.4715
1640	0.38830	335.76	0.15339	1.5252

Table 3 (continued)

Temperature (°R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy [$Btu \cdot lb^{-1} \cdot (°R)^{-1}$]	Specific Volume (ft^3/lb)
At a Pressure of 60 psia				
1660	0.42164	345.56	0.15929	1.5809
1680	0.45570	355.51	0.16521	1.6382
1700	0.49016	365.53	0.17111	1.6970
1720	0.52471	375.57	0.17695	1.7567
1740	0.55899	385.56	0.18269	1.8171
1760	0.59269	395.44	0.18830	1.8777
1780	0.62547	405.13	0.19374	1.9382
1800	0.65706	414.58	0.19899	1.9981
1820	0.68721	423.75	0.20403	2.0570
1840	0.71573	432.59	0.20883	2.1148
1860	0.74248	441.07	0.21340	2.1711
1880	0.76737	449.19	0.21771	2.2258
1900	0.79036	456.92	0.22178	2.2787
1920	0.81146	464.28	0.22562	2.3298
1940	0.83070	471.27	0.22922	2.3791
1960	0.84818	477.91	0.23261	2.4266
1980	0.86397	484.21	0.23579	2.4723
2000	0.87819	490.19	0.23878	2.5163
At a Pressure of 100 psia				
900	0.00039	141.82	0.00301	0.36188
920	0.00054	145.00	0.00647	0.36998
940	0.00074	148.19	0.00986	0.37809
960	0.00099	151.39	0.01320	0.38624
980	0.00132	154.61	0.01648	0.39441
1000	0.00174	157.84	0.01971	0.40263
1020	0.00226	161.10	0.02290	0.41090
1040	0.00291	164.38	0.02605	0.41923
1060	0.00371	167.69	0.02918	0.42763
1080	0.00470	171.03	0.03228	0.43613
1100	0.00589	174.42	0.03536	0.44473
1120	0.00732	177.86	0.03842	0.45346
1140	0.00904	181.35	0.04149	0.46234
1160	0.01107	184.90	0.04455	0.47140
1180	0.01346	188.53	0.04763	0.48067
1200	0.01627	192.24	0.05072	0.49017
1220	0.01955	196.05	0.05383	0.49994
1240	0.02334	199.95	0.05698	0.51003
1260	0.02770	203.97	0.06018	0.52047
1280	0.03271	208.12	0.06342	0.53130
1300	0.03843	212.41	0.06672	0.54259
1320	0.04491	216.86	0.07009	0.55438
1340	0.05225	221.47	0.07353	0.56673
1360	0.06051	226.27	0.07706	0.57970
1380	0.06976	231.26	0.08068	0.59336

Table 3 (continued)

Temperature (°R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy $[Btu \cdot lb^{-1} \cdot (°R)^{-1}]$	Specific Volume (ft^3/lb)
		At a Pressure of 100 psia		
1400	0.08009	236.47	0.08440	0.60777
1420	0.09156	241.91	0.08823	0.62301
1440	0.10426	247.60	0.09218	0.63913
1460	0.11827	253.54	0.09625	0.65623
1480	0.13363	259.76	0.10045	0.67436
1500	0.15043	266.26	0.10478	0.69359
1520	0.16870	273.05	0.10925	0.71401
1540	0.18849	280.15	0.11386	0.73565
1560	0.20982	287.56	0.11861	0.75858
1580	0.23270	295.27	0.12349	0.78284
1600	0.25711	303.29	0.12850	0.80844
1620	0.28299	311.60	0.13363	0.83540
1640	0.31029	320.20	0.13887	0.86370
1660	0.33888	329.05	0.14421	0.89331
1680	0.36862	338.14	0.14961	0.92416
1700	0.39935	347.42	0.15507	0.95616
1720	0.43085	356.85	0.16056	0.98919
1740	0.46289	366.39	0.16604	1.0230
1760	0.49520	375.99	0.17149	1.0577
1780	0.52752	385.59	0.17689	1.0928
1800	0.55956	395.13	0.18219	1.1283
1820	0.59106	404.56	0.18737	1.1639
1840	0.62176	413.84	0.19241	1.1993
1860	0.65141	422.90	0.19729	1.2346
1880	0.67984	431.72	0.20198	1.2693
1900	0.70686	440.26	0.20647	1.3034
1920	0.73235	448.50	0.21076	1.3368
1940	0.75624	456.42	0.21484	1.3694
1960	0.77849	464.00	0.21871	1.4010
1980	0.79907	471.26	0.22238	1.4317
2000	0.81802	478.19	0.22584	1.4614
		At a Pressure of 150 psia		
900	0.00032	141.81	0.00000	0.24123
920	0.00044	144.98	0.00344	0.24662
940	0.00060	148.17	0.00683	0.25203
960	0.00081	151.36	0.01015	0.25744
980	0.00108	154.56	0.01342	0.26288
1000	0.00142	157.78	0.01664	0.26833
1020	0.00184	161.01	0.01981	0.27382
1040	0.00238	164.27	0.02295	0.27933
1060	0.00303	167.55	0.02604	0.28489
1080	0.00383	170.86	0.02910	0.29050
1100	0.00481	174.21	0.03215	0.29617
1120	0.00598	177.59	0.03517	0.30190

Table 3 (continued)

Temperature (°R)	Weight Fraction of $AlCl_3$	Enthalpy (Btu/lb)	Entropy [Btu·lb^{-1}·(°R)$^{-1}$]	Specific Volume (ft^3/lb)
		At a Pressure of 150 psia		
1140	0.00738	181.02	0.03817	0.30772
1160	0.00904	184.50	0.04117	0.31364
1180	0.01099	188.04	0.04418	0.31966
1200	0.01328	191.65	0.04718	0.32582
1220	0.01596	195.33	0.05020	0.33212
1240	0.01906	199.10	0.05324	0.33859
1260	0.02262	202.96	0.05630	0.34526
1280	0.02671	206.92	0.05940	0.35214
1300	0.03138	211.01	0.06254	0.35927
1320	0.03668	215.21	0.06573	0.36668
1340	0.04268	219.56	0.06897	0.37438
1360	0.04943	224.06	0.07228	0.38243
1380	0.05700	228.72	0.07566	0.39086
1400	0.06546	233.56	0.07911	0.39969
1420	0.07487	238.58	0.08265	0.40898
1440	0.08529	243.81	0.08628	0.41876
1460	0.09679	249.26	0.09001	0.42908
1480	0.10944	254.93	0.09385	0.43997
1500	0.12329	260.84	0.09779	0.45149
1520	0.13840	267.01	0.10184	0.46366
1540	0.15482	273.43	0.10602	0.47654
1560	0.17259	280.13	0.11031	0.49016
1580	0.19174	287.10	0.11472	0.50455
1600	0.21228	294.35	0.11925	0.51974
1620	0.23421	301.87	0.12389	0.53576
1640	0.25751	309.67	0.12865	0.55261
1660	0.28214	317.73	0.13351	0.57031
1680	0.30804	326.05	0.13846	0.58883
1700	0.33510	334.60	0.14349	0.60817
1720	0.36320	343.36	0.14858	0.62828
1740	0.39221	352.29	0.15371	0.64911
1760	0.42194	361.37	0.15887	0.67059
1780	0.45220	370.56	0.16403	0.69264
1800	0.48277	379.81	0.16917	0.71517
1820	0.51342	389.07	0.17426	0.73806
1840	0.54391	398.31	0.17928	0.76121
1860	0.57402	407.46	0.18420	0.78449
1880	0.60352	416.50	0.18901	0.80778
1900	0.63219	425.37	0.19368	0.83097
1920	0.65985	434.04	0.19819	0.85395
1940	0.68635	442.47	0.20254	0.87662
1960	0.71155	450.65	0.20671	0.89890
1980	0.73537	458.55	0.21070	0.92071
2000	0.75774	466.17	0.21451	0.94200

(ref 15) are listed in Table 4. Aluminum chloride is stable on a free-energy basis relative to these pure container materials. If, however, the products of a possible corrosion reaction are gaseous or form a solid or liquid solution and if a mechanism exists for the removal of the reaction products from the region of the reaction, a corrosion reaction might proceed. Unfortunately aluminum exists in two positive valence states. The chlorides AlCl and $AlCl_3$ are both gaseous in the temperature range of interest.

Table 4. Free Energies of Formation of Aluminum Chloride and the Chlorides of Some Possible Container Materials

Metal Chloride	Free Energy of Formation (kcal per mole of Cl)	
	At 500°K	At 1000°K
$AlCl_3$	−48(*g*)	−46(*g*)
$CrCl_3$	−35	−26
$CrCl_2$	−40	−32
$FeCl_3$	−23	−21
$FeCl_2$	−33	−27
$NiCl_2$	−27	−18
AlCl	−22(*g*)	−32(*g*)
$MoCl_2$	−15	−8
$MoCl_3$	−14	−6
$MoCl_4$	−12	−7
$MoCl_5$	−10	−7
$MoCl_6$	−7	−3

As an illustration of the possible corrosion behavior, the corrosion of an alloy containing chromium and nickel in a system in which gaseous aluminum chloride is circulated at temperatures in the range 500 to 1000°K is discussed here. The most likely corrosion reactions involving chromium are:

Reaction A

$$\tfrac{2}{3}AlCl_3(g) + Cr \rightleftharpoons CrCl_2(s) + \tfrac{2}{3}Al$$

$$\Delta F^\circ \text{ at } 500^\circ K = +16 \text{ kcal}$$

$$\Delta F^\circ \text{ at } 1000^\circ K = +28 \text{ kcal}$$

Reaction B

$$AlCl_3(g) + Cr \rightleftharpoons AlCl(g) + CrCl_2(s)$$

$$\Delta F^\circ \text{ at } 500^\circ K = +42 \text{ kcal}$$

$$\Delta F^\circ \text{ at } 1000^\circ K = +42 \text{ kcal}$$

Reaction C

$$3AlCl(g) \rightleftharpoons 2Al + AlCl_3(g)$$

$$\Delta F^\circ \text{ at } 500^\circ K = -78 \text{ kcal}$$

$$\Delta F^\circ \text{ at } 1000^\circ K = -42 \text{ kcal}$$

The equilibrium constant, *K*, for reaction A is

$$K_A = e^{-\Delta F/RT} = \frac{a_{Al}^{2/3}\, a_{CrCl_2}}{P_{AlCl_3}^{2/3}\, a_{Cr}} \qquad (19)$$

$$= 10^{-7} \text{ at } 500^\circ K$$

$$= 10^{-6.1} \text{ at } 1000^\circ K \ .$$

If pure aluminum is produced from the reaction of pure chromium and $AlCl_3$ at a pressure of 1 atm, the activity of $CrCl_2$, a_{CrCl_2}, is $10^{-6.1}$ at 1000°K and 10^{-7} at 500°K. The partial pressure of $CrCl_2$ under these conditions, P_{CrCl_2}, may be calculated from the relation

$$P_{CrCl_2} = a_{CrCl_2} P^0_{CrCl_2} \ , \qquad (20)$$

where $P^0_{CrCl_2}$ is the vapor pressure of the pure solid, which may be calculated from the relation[11]

$$\log P^0_{CrCl_2}\ (\text{atm}) = \frac{-14{,}000}{T} - 0.62 \log T - 0.00058T + 12.26 \ . \qquad (21)$$

The vapor pressure $P^0_{CrCl_2}$ is $10^{-4.18}$ or 6.6×10^{-5} atm at 1000°K and $10^{-17.70}$ or 2×10^{-18} atm at 500°K. The calculated partial pressures of $CrCl_2$ under the stated conditions are then 5.3×10^{-11} atm at 1000°K and 2×10^{-25} atm at 500°K. In a system in which aluminum chloride gas was being

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[15] A. Glassner, *The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K*, ANL-5750 (1957).

circulated, if reaction A were the only significant one, it would take a minimum of 2×10^{10} moles of aluminum chloride gas to move 1 mole of $CrCl_2$ from the hot zone and deposit it as solid $CrCl_2$ in the cold zone. The fact that the aluminum metal produced in reaction A might form a solid solution with the metal wall in the reaction zone would increase the initial partial pressure and transport of $CrCl_2$. After an initial deposit of aluminum metal had formed on the surface, the reaction would yield a smaller partial pressure of $CrCl_2$, with diffusion of aluminum into the metal in the hot zone being one controlling factor for this partial pressure if reaction A were important. Not only is the initial activity of chromium in an alloy lower than that of the pure metal, but the depletion of the surface chromium concentration would further lower the activity of chromium at the surface and, hence, lower the maximum partial pressure of $CrCl_2$ in the circulating gas at the hot end. This would lead to a smaller transport of $CrCl_2$ from the hot to the cold zone. The chromium concentration on the reaction surface and, hence, the corrosion rate, would then be controlled by the diffusion of chromium to the surface in the hot zone. This diffusion would be a second controlling factor if reaction A were important.

The equilibrium constant for reaction B is

$$K_B = e^{-\Delta F/RT} = \frac{P_{\mathrm{AlCl}}\,a_{\mathrm{CrCl_2}}}{P_{\mathrm{AlCl_3}}\,a_{\mathrm{Cr}}} = \frac{P_{\mathrm{AlCl}}\,P_{\mathrm{CrCl_2}}}{P_{\mathrm{AlCl_3}}\,a_{\mathrm{Cr}}\,P^0_{\mathrm{CrCl_2}}} \qquad (22)$$

$$= 10^{-18.4} \text{ at } 500^\circ\mathrm{K}$$

$$= 10^{-9.2} \text{ at } 1000^\circ\mathrm{K} \ .$$

For pure chromium exposed to aluminum chloride at a pressure of 1 atm,

$$P_{\mathrm{AlCl}}P_{\mathrm{CrCl_2}} = 10^{-9.2} \times 10^{-4.18} = 10^{-13.4}$$

at 1000°K and

$$P_{\mathrm{AlCl}} = P_{\mathrm{CrCl_2}} = 10^{-6.7} \text{ or } 2 \times 10^{-7} \ .$$

This partial pressure is higher than that which would be present above a chromium-containing alloy in which the activity of the chromium was lower than the activity of pure chromium metal. The partial pressure of $CrCl_2$ from reaction B is higher than that from reaction A. Reaction B should be, therefore, the important corrosion reaction and should result in the transport, at the very most, of about 2×10^{-7} mole of chromium per mole of circulating gas. At the low-temperature zone, $CrCl_2$ will initially deposit as the solid, AlCl will disproportionate according to reaction C, and a small concentration of aluminum will deposit on the surface of the alloy. After a small activity of aluminum is built up in the metal, the reaction at the low-temperature zone should be the reverse of reaction B, with chromium metal being deposited on the walls. At the hot zone, after the surface chromium has been depleted, the reaction will be limited by the diffusion of chromium from the interior of the metal to the surface. If reaction B is important, this diffusion of chromium to the surface at the hot zone will probably be the rate-controlling step in the transport of chromium metal from the hot to the cold zone. Lowering the temperature of the hot zone would decrease the rate of corrosion, mainly by lowering the diffusion rate of chromium. The formation of an adherent nonmetallic film on the surface that is not attacked by aluminum chloride would also decrease the corrosion rate.

The corrosion of nickel would be much less severe. The reactions significant for nickel corrosion are:

Reaction D

$$\tfrac{2}{3}\mathrm{AlCl_3}(g) + \mathrm{Ni} \rightleftharpoons \mathrm{NiCl_2}(s) + \tfrac{2}{3}\mathrm{Al}$$

$$\Delta F^\circ \text{ at } 500^\circ\mathrm{K} = +42 \text{ kcal}$$

$$\Delta F^\circ \text{ at } 1000^\circ\mathrm{K} = +56 \text{ kcal}$$

Reaction E

$$\mathrm{AlCl_3}(g) + \mathrm{Ni} \rightleftharpoons \mathrm{AlCl}(g) + \mathrm{NiCl_2}(s)$$

$$\Delta F^\circ \text{ at } 500^\circ\mathrm{K} = +68 \text{ kcal}$$

$$\Delta F^\circ \text{ at } 1000^\circ\mathrm{K} = +70 \text{ kcal}$$

The equilibrium constants for reactions D and E are:

$$K_D = e^{-\Delta F/RT} = \frac{a_{\mathrm{Al}}^{2/3}\, a_{\mathrm{NiCl_2}}}{a_{\mathrm{Ni}}\, P_{\mathrm{AlCl_3}}^{2/3}}$$

$$= \frac{a_{\mathrm{Al}}^{2/3}\, P_{\mathrm{NiCl_2}}}{a_{\mathrm{Ni}}\, P_{\mathrm{AlCl_3}}^{2/3}\, P_{\mathrm{NiCl_2}}^{0}} \qquad (23)$$

$$= 10^{-18.4} \text{ at } 500^{\circ}\mathrm{K}$$

$$= 10^{-12.2} \text{ at } 1000^{\circ}\mathrm{K} \;,$$

$$K_E = e^{-\Delta F/RT} = \frac{P_{\mathrm{AlCl}}\, a_{\mathrm{NiCl_2}}}{P_{\mathrm{AlCl_3}}\, a_{\mathrm{Ni}}}$$

$$= \frac{P_{\mathrm{AlCl}}\, P_{\mathrm{NiCl_2}}}{a_{\mathrm{Ni}}\, P_{\mathrm{AlCl_3}}\, P_{\mathrm{NiCl_2}}^{0}} \qquad (24)$$

$$= 10^{-29.8} \text{ at } 500^{\circ}\mathrm{K}$$

$$= 10^{-15.3} \text{ at } 1000^{\circ}\mathrm{K} \;.$$

The vapor pressure of pure $NiCl_2$, $P^0_{\mathrm{NiCl_2}}$, may be calculated from the equation[11]

$$\log P^0_{\mathrm{NiCl_2}}\,(\mathrm{atm}) = \frac{-13{,}300}{T} - 2.68 \log T + 19.00 \;. \qquad (25)$$

At 1000°K, $P^0_{\mathrm{NiCl_2}}$ is $10^{-2.34}$ or 4.6×10^{-3} atm and at 500°K it is $10^{-14.83}$ or 1.5×10^{-15} atm. At the high-temperature zone, reaction E leads to a higher partial pressure of $NiCl_2$ than does reaction D. For the corrosion of pure nickel,

$$P_{\mathrm{NiCl_2}} = P_{\mathrm{AlCl}}$$

$$= (10^{-15.3} \times 10^{-2.3})^{1/2}$$

$$= 10^{-8.8} \text{ or } 1.6 \times 10^{-9} \text{ atm} \;.$$

At the low-temperature zone, the reverse of reaction E will probably take place, and nickel metal will deposit on the surface. The limiting factor in the corrosion of nickel from an alloy composed principally of nickel would be the total volume of gas passing over the surface. One mole of nickel would be transported per 6×10^8 moles of gas at 1 atm passing the surface at 1000°K. One mole of $AlCl_3$ transports roughly 20 kcal of heat in going from 1000 to 500°K, so about 1 mole of nickel would be transported per 1.2×10^{10} kcal, 1.4×10^7 kwhr, or about 600 Mwd of heat. The transport corrosion of iron and molybdenum as minor constituents of an alloy should be less than that of chromium.

In conclusion, corrosion of an alloy composed mainly of nickel and containing some chromium might not be negligible for long-term operation of a system circulating gaseous aluminum chloride at temperatures in the range 500 and 1000°K, but the corrosion would be small enough for short-term operation of such a system. The corrosion rate could be decreased considerably by operating with the hot zone of the loop at temperatures lower than the 1000°K for which these calculations were made or by the formation of an oxide coating on the surface of the metal. The estimated values of the thermal conductivity, heat capacity, and viscosity indicate that aluminum chloride may be a unique gaseous heat exchange medium that requires very low pumping power. It should be emphasized that these are crude estimates based on a limited amount of data of varying degrees of reliability. Although a conscious attempt has been made to make these estimates conservative, some of the estimates should be checked experimentally.

ENGINEERING PROBLEMS OF SOME TYPICAL APPLICATIONS

Where aluminum chloride vapor is used as a working fluid in a thermodynamic cycle or as a heat transfer medium, the pressures and temperatures must be carefully chosen to exploit to the fullest the extra performance obtainable from dissociation. Normally a temperature range will be defined by the structural strength of the metals in the system or by other considerations, such as corrosion, so that the only variable available to the designer will be the pressure. This means that the pressure level must be chosen with care to give the best over-all system design. It is likely that it will be necessary to compromise the design of other components if the fullest benefits are to be derived from the use of aluminum chloride.

Aluminum Chloride as a Heat Transfer Medium

A typical application for which aluminum chloride may have promise is as an intermediate heat transfer fluid between the fluoride fuel of a molten-salt-fueled reactor and the steam generator. The use of a gas rather than a liquid in the intermediate loop would facilitate removal of the heat transfer medium; it would not be necessary to design the system to avoid the presence of low spots which would present difficult drainage or scavenge problems. It would make possible the placing of flanged joints in cool zones at the top of the system and outside of the heat exchanger pressure envelope so that leaks of the molten fuel into the aluminum chloride would be contained within the pressure envelope. The pressure required, namely, 20 to 60 psi in the aluminum chloride, would present no serious structural problems in the design of the containing vessel. From Fig. 4, which is a plot of data obtained from Eq. (7), it is evident that there would be no solid aluminum chloride precipitated at the temperatures and pressures prevailing in a molten-salt-fueled reactor. . Aluminum chloride would have the advantage as a heat transfer fluid that it would be chemically inert relative to either the molten salt or water. This would make it desirable from the hazards standpoint and would give a system relatively insensitive to leaks between any two sets of fluid; that is, a small leak from one system into another would not lead to the formation of a set of deposits which would be very difficult to remove. It would be necessary, of course, to make the steam generator, as well as the fuel–to–aluminum chloride heat exchanger, of a relatively expensive high-nickel-content alloy.

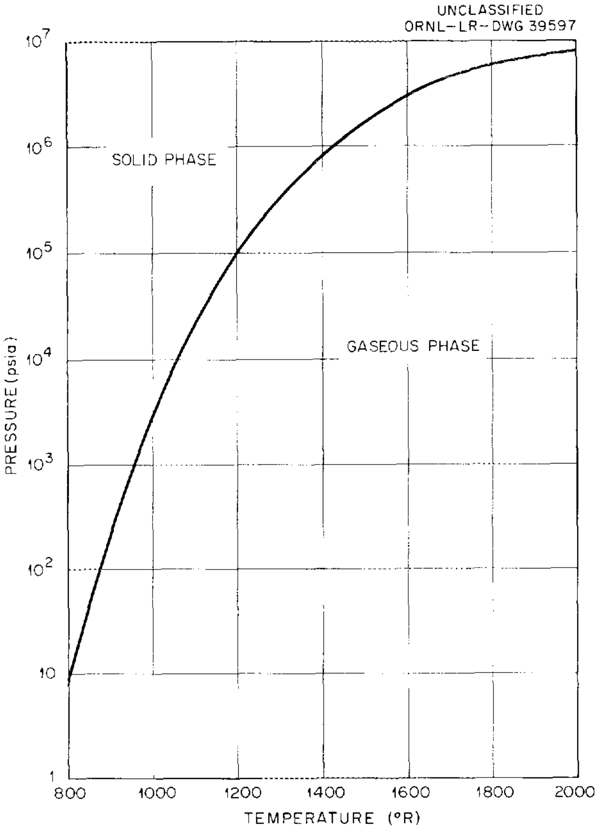

Fig. 4. Gas-Solid Equilibrium Diagram for Aluminum Chloride.

The principal disadvantage of this arrangement is that it would require a larger amount of heat transfer surface area and a higher pumping power than would be the case for an inert molten salt, for example. However, it would have a major advantage in that there would be no freezing problem in the intermediate heat exchanger circuit. The freezing problem presents exceedingly difficult design problems if a fluid such as sodium or NaK is employed as the intermediate heat transfer medium.

The temperature range for such an application is lower than is desirable in that the heat transfer surfaces for the molten salt would be at about 1100 to 1200°F, while those in the steam generator would be at 700 to 1000°F. As may be seen in Fig. 1, this temperature range is below that which gives the maximum obtainable average effective specific heat if the pressure is maintained high enough (30 to 100 psi) to keep pumping losses to acceptable levels.

Aluminum Chloride Vapor in a Gas-Turbine Cycle

The features of a gas-turbine cycle utilizing aluminum chloride deserve special attention. The cycle contemplated is indicated schematically in Fig. 5. The pressures and temperatures should be chosen so that the gas will be mostly in the form of Al_2Cl_6 during compression, while during the expansion process it will be mostly $AlCl_3$. This, in effect, will cut the compression work roughly in half and thus produce a marked improvement in cycle efficiency. The nature of this effect can be visualized readily by examining the P-V diagrams of Fig. 6, which compare similar ideal gas-turbine cycles for helium, aluminum chloride, and water. It should be remembered that the work involved in each compression or expansion process is directly proportional to the area of the P-V diagram, and the net work is

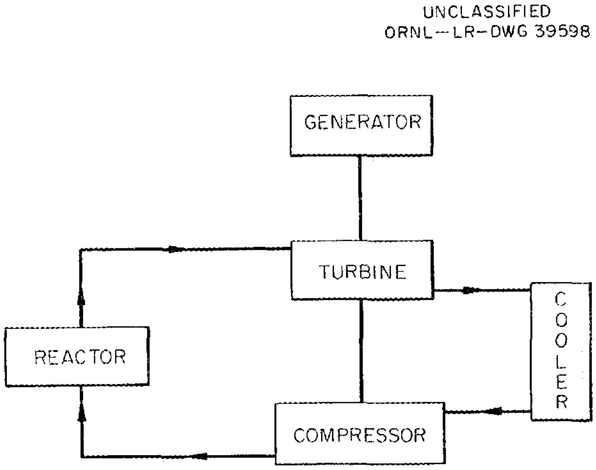

Fig. 5. Aluminum Chloride Gas-Turbine Cycle.

proportional to the net area for the cycle. The Rankine cycle utilizing water vapor was included in Fig. 6 to show that the proposed aluminum chloride cycle is between a gas-turbine (or Brayton) cycle utilizing helium and a Rankine cycle utilizing water in its requirements for work input during the compression process.

The diagrams of Fig. 6 were prepared for ideal cycles with no allowances for losses. The most important of these losses are associated with the efficiencies of the compressor and the turbine, which are likely to be of the order of 85%. This means that, with an 85% efficient compressor, the ideal work input will be 85% of the actual work input, while the actual work output of the turbine will be only 85% of the ideal. In addition, pressure drops between the compressor and the turbine will

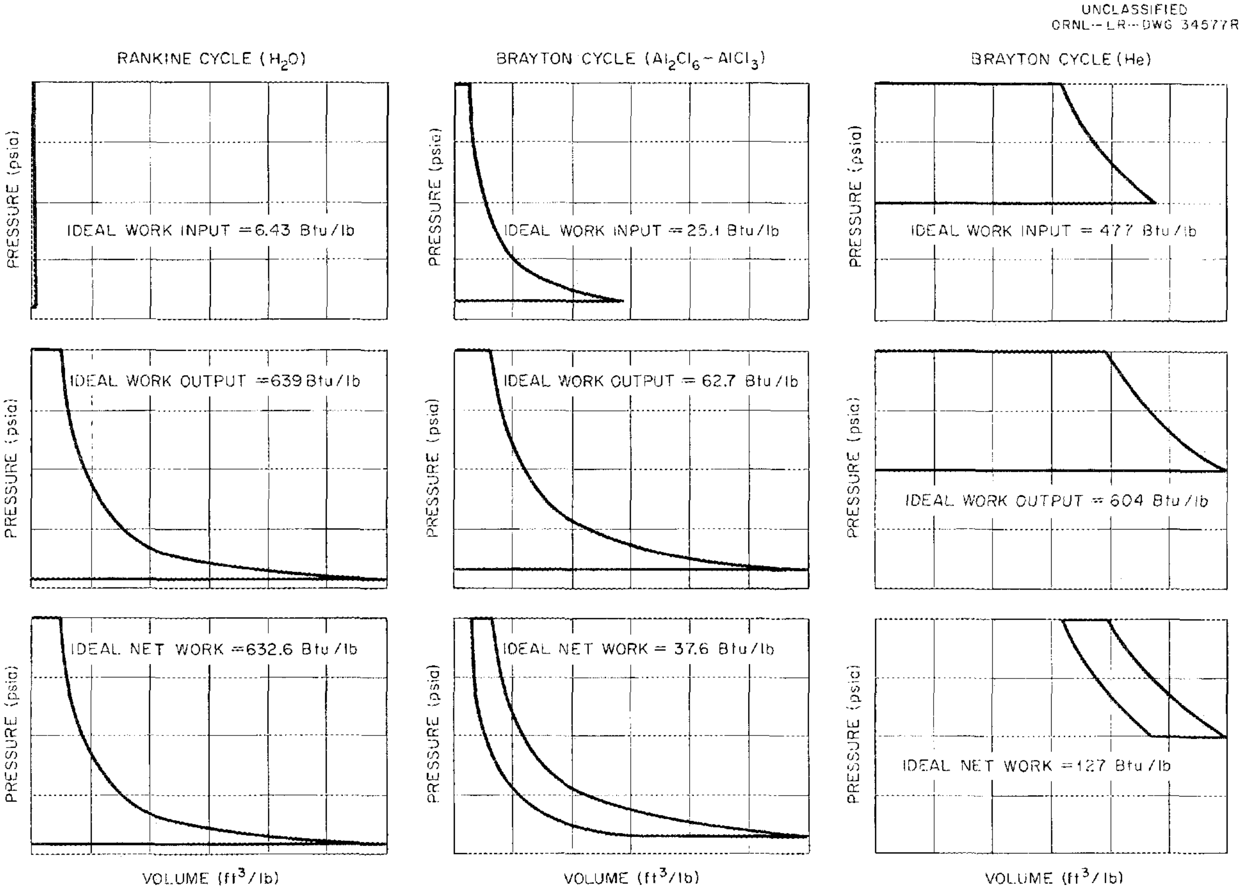

Fig. 6. P-V Diagrams for Typical Ideal Thermodynamic Cycles.

also cause major losses in net output from the cycle. The nature of these effects can be seen readily in Fig. 7. It should be emphasized that the shaded portions of these diagrams are merely proportional to the losses they represent and that the actual paths of the processes cannot be shown. A rough allowance for these pressure losses can be made by using lower values for the turbine and compressor efficiencies, for example, 80% in each case.

If allowances are made for these losses to obtain the actual net outputs for the cycles of Fig. 6, the diagrams of Fig. 8 result. The relatively large work input required for the compression process of the Brayton cycle makes the cycle efficiency very sensitive to compressor inlet temperature because the compression work increases rapidly with temperature. As a result, the net work output and over-all cycle efficiency of the Brayton cycle drop off so rapidly with increasing temperature at the compressor inlet that, for any practicable plant, the compressor inlet temperature must be held below 150°F if conventional working fluids are used. At the same time, the turbine inlet temperature must be at least 1200°F, and preferably should be above 1400°F if there is to be an appreciable positive net area for the P-V diagram.

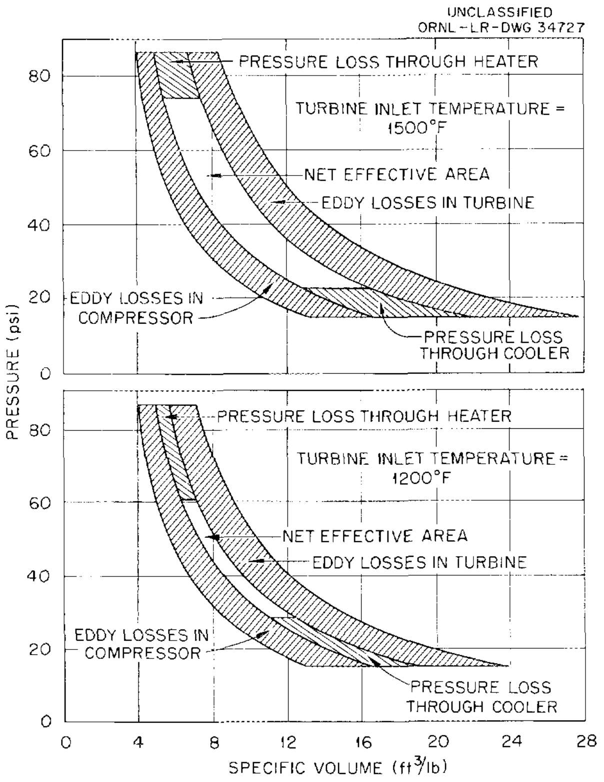

Fig. 7. P-V Diagrams for Ideal Gas Turbine Air Cycles with Cross-Hatched Areas to Indicate the Magnitude of the Principal Losses.

The unusual properties of aluminum chloride make it possible to go to higher compressor inlet temperatures than with other fluids. The effects of variations in both the compressor inlet temperature and the compressor pressure ratio are indicated in Fig. 9 for a turbine inlet temperature of 1540°F. While this temperature is high by steam power plant standards, the much lower pressures in the aluminum chloride system reduce stresses sufficiently to compensate for most of the temperature difference. In any event, it is necessary to go to peak temperatures in this range to take full advantage of the unusual properties of the aluminum chloride. It is evident from Fig. 9 that the aluminum chloride vapor cycle should be designed for a compressor inlet temperature of around 540 to 640°F and a pressure ratio of 20 to 40. Further lowering of the compressor inlet temperature will do little to enhance efficiency, since at 540°F most of the gas is in the dimer state already.

A point of interest is that it was found in the cycle analysis that during the compression and expansion processes there was little change in the percentage of the gas dissociated. This will simplify the design of compressors and turbines for such an application.

The heat transfer coefficient for the aluminum chloride is sufficiently high for the high-pressure portion of the cycle, and therefore good heat transfer could be obtained in a reactor core. In the cooler, however, the heat transfer performance of the aluminum chloride would be poor, and a large surface area would be required. The poor heat transfer coefficient of aluminum chloride in the cooler stems from the fact that the pressure at the turbine outlet would be only approximately 1/10 atm, and this would give a low Reynolds number. The pressure ahead of the turbine, on the other hand, would be 20 to 40 times greater, which would give heat transfer coefficients correspondingly higher.

Binary Vapor Cycle Applications

If aluminum chloride were used as a reactor coolant or as an intermediate heat transfer fluid

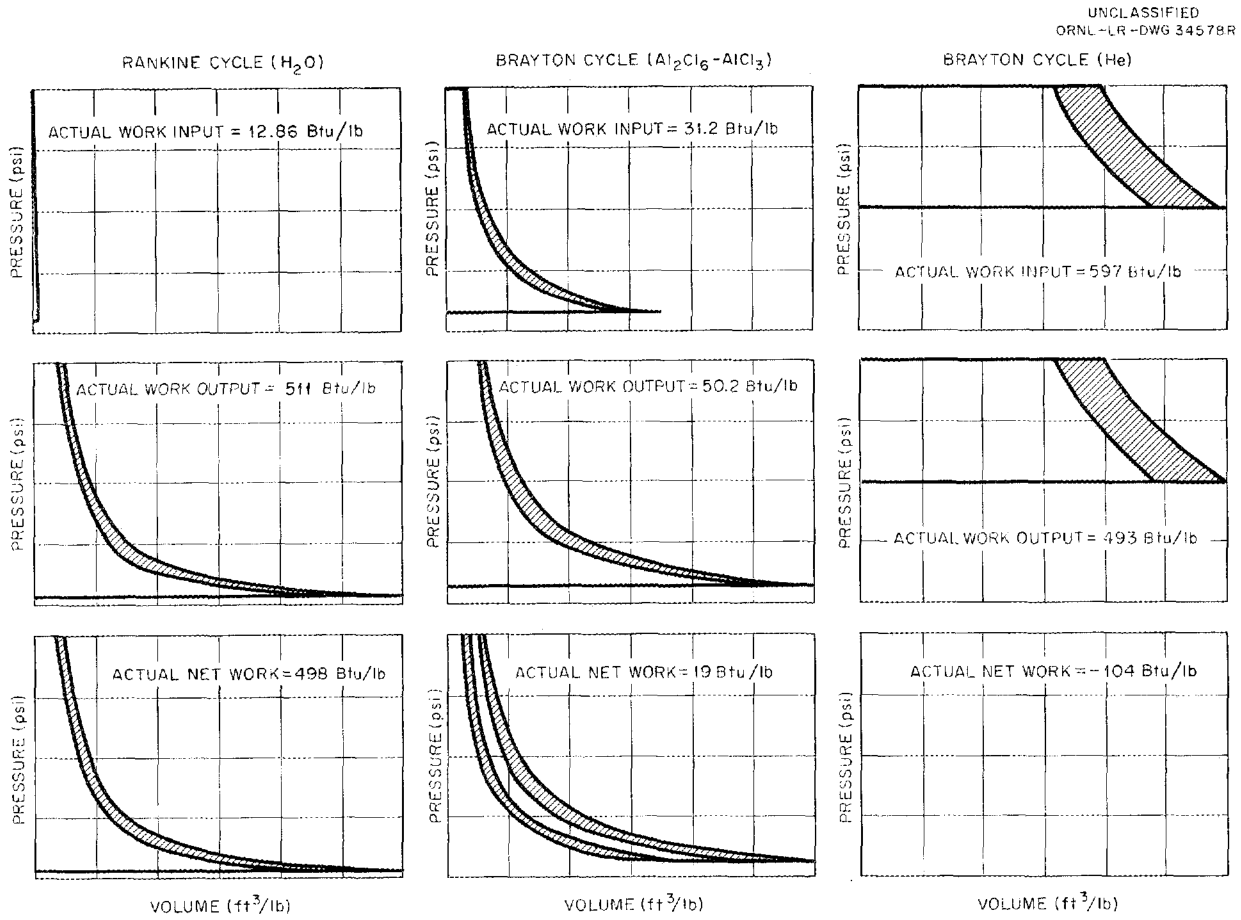

Fig. 8. P-V Diagrams for Typical Ideal Thermodynamic Cycles with Cross-Hatched Areas to Represent the Losses Entailed by Compressor and Turbine Efficiencies of 80%.

for a molten-salt-fueled reactor, it appears that a binary vapor cycle employing aluminum chloride in the high-temperature portion and water vapor in the lower-temperature region ought to be considered. Such a cycle would resemble in many ways the binary mercury vapor–steam cycle which has been used in a number of U.S. power plants. It would have the advantage that it would permit operation at high temperatures (which would be advantageous from the thermodynamic standpoint) while avoiding the expense associated with the high pressures characteristic of high-temperature steam cycles. While there are a host of different combinations of conditions that might be employed, a typical case is presented in Table 5. The aluminum chloride would be expanded through a turbine similar to that described above. The cooler for the aluminum chloride would also serve as the boiler and superheater for the steam system. It may be seen from Table 5 that this system gives a very much higher over-all thermal efficiency than is obtainable from the gas-turbine cycle alone. A corresponding steam system designed for a pressure of 2400 psi and a peak temperature out of the superheater of 1050°F would give an over-all thermal efficiency of about 38%, somewhat less than the efficiency that the typical binary vapor cycle chosen would attain.

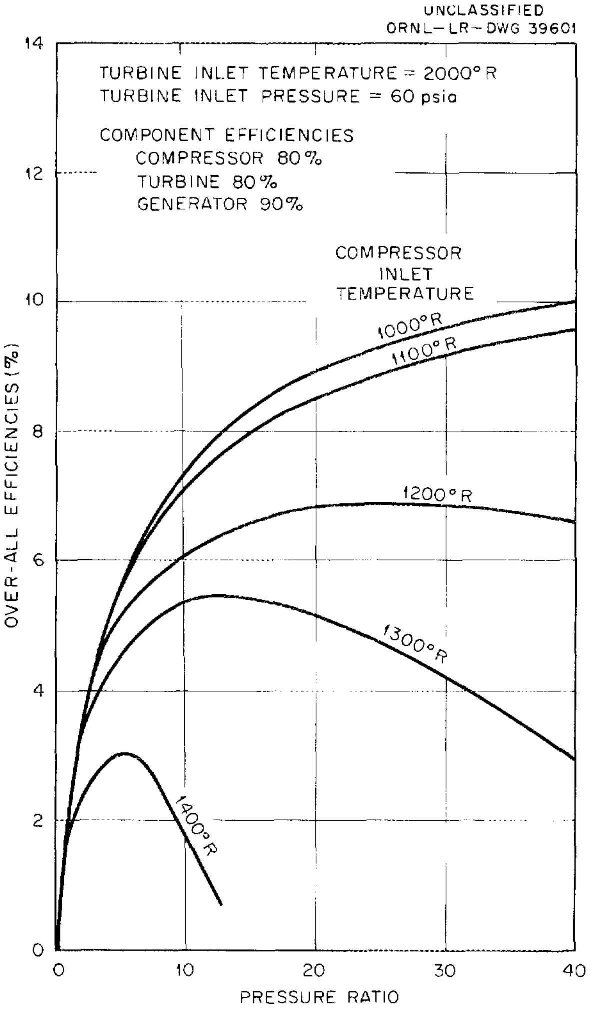

Fig. 9. Cycle Efficiency vs Pressure Ratio for $AlCl_3$.

CONCLUSIONS

Thermodynamic data have been prepared and are presented in the form of tables and charts to facilitate engineering calculations on systems employing aluminum chloride vapor either as a heat transfer medium or as the working fluid in a thermodynamic cycle. A number of typical applications have been considered, but in none of these has the aluminum chloride shown outstanding advantages over more conventional media. However, it is believed that for some special applications it may well prove to have some outstanding advantages where the characteristics of the other system components are such as to make it possible to exploit to the fullest the unique characteristics of aluminum chloride.

Table 5. Binary Vapor Cycle

Ideal mass ratio = 0.18487 lb of water per lb of aluminum chloride
Actual mass ratio = 0.19585 lb of water per lb of aluminum chloride

Ideal cycle efficiency = 53.2%
Actual cycle efficiency = 41.4%

Condition	Temperature (°F)	Enthalpy (Btu/lb)	Entropy (Btu/°F)	Pressure (psia)	Specific Volume (ft^3/lb)	Weight Fraction Dissociated or Steam Quality
			Aluminum Chloride			
Compressor inlet	440	142	0.02530	5	7.2476	0.00176
Compressor outlet (isentropic)	570	164	0.02530	100	0.41506	0.00259
Compressor outlet (80% efficiency)	615	169.5	0.0311	100	0.4344	0.00447
Turbine inlet	1540	478	0.22584	100	1.4614	0.818
Turbine outlet (isentropic)	1150	406	0.22584	5	23.07	0.781
Turbine outlet (80% efficiency)	1175	420.4	0.2343	5	23.92	0.818
			Steam*			
Pump inlet	91.72	59.71	0.1147	0.7368	0.01611	Saturated liquid
Pump outlet (isentropic)	91.72	66.14	0.1147	2400	0.01600	Compressed liquid
Pump outlet (50% efficiency)	91.72	72.57	0.1243	2400	0.01600	Compressed liquid
Turbine inlet	1050	1494	1.5554	2400	0.3373	Superheated vapor
Turbine outlet (isentropic)	91.72	855	1.5554	0.7368	339.5	0.763
Turbine outlet (80% efficiency)	91.72	983	1.790	0.7368	394.2	0.886

*The bases for enthalpy and entropy of aluminum chloride and steam are not the same. Hence comparison of the absolute values of these properties between the two fluids is meaningless.

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