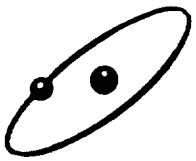
"FINDING THE PROPERTIES OF HYDROGEN MIXTURES"

EB 61-11 7-7-61

Here are data you need for solving those fluid flow and heat transfer problems. This short-cut method helps determine physical properties.

How to Cope With Hydrogen



Finding the Properties of Hydrogen Mixtures

Viscosity
Thermal Conductivity
Specific Heat Density

THIS SPECIAL report on hydrogen presents a wealth of useful data and information. While it does not give the answers to all problems associated with hydrogen it does help in process design, mechanical design and maintenance.

The effect of hydrogen on the physical properties of gas mixtures is out of proportion to its size and weight. The determination of physical properties of these mixtures is essential in process calculations. The influence of hydrogen is especially great in fluid flow and heat transfer problems. This special report presents theoretical and practical equations for solving these everyday problems. The collection of graphical data represents hours of literature searching.

One major problem associated with hydrogen attack is the recognization of the particular type. Only after suitable classification can the seriousness of the attack be determined and preventative maintenance planned. The theory of hydrogen attack and the classification of the various types are presented in this special report.

Hydrogen embrittlement is a very insidious phenomenon. Without any previous warning it may exhibit itself with a dramatic equipment failure. This report describes some empirical observations useful in determining hydrogen embrittlement.

All hydrogen problems cannot be solved by the use of high-powered alloys. This report tells the uses and limitations of the presently available alloys and steels. This knowledge is money. Reported here are the characteristics imparted to a steel by the use of various alloying elements. Proper use of these materials can solve the problems of hydrogen blistering, decarburization and cracking.

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HEAT TRANSFER and fluid flow calculations for mixtures containing hydrogen can be made in normal fashion provided one can evaluate properly the viscosity, thermal conductivity, specific heat, and density of the mixture. This article presents methods for making such calculations.

Process calculations involving mixtures containing hydrogen present problems to engineers. Hydrogen has the lowest molecular weight of any substance. Thus the mixture containing a very low weight percent of hydrogen contains a significant volume percentage of hydrogen. The physical properties of hydrogen differ considerably from those of the hydrocarbons and more common gases.

- Specific heat is approximately 3.5 as compared to a more conventional range of 0.25 to 1.0.
- Thermal conductivity is approximately 4 to 10 times greater than that of the more common process fluids.
- Viscosity of hydrogen is somewhat lower than that of the other common fluids.

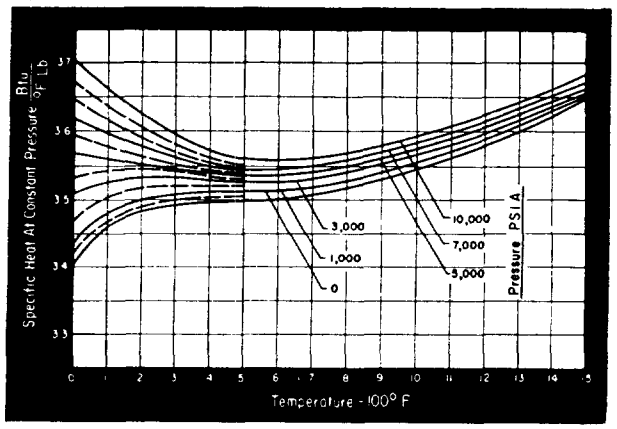


FIGURE 1—Specific heat of hydrogen.

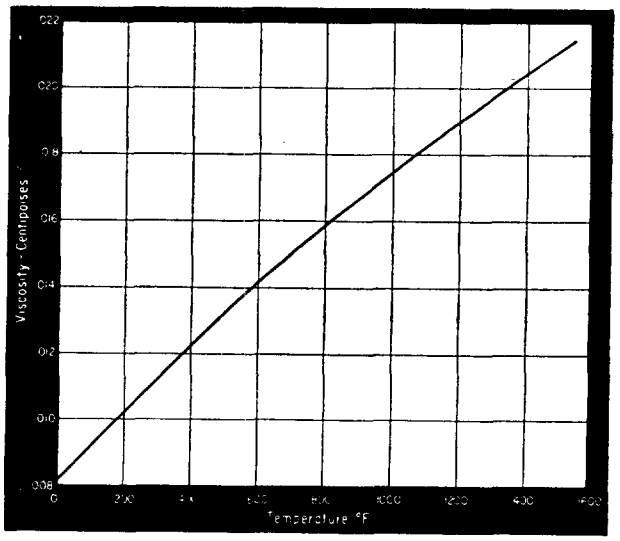


FIGURE 3—Viscosity of hydrogen.

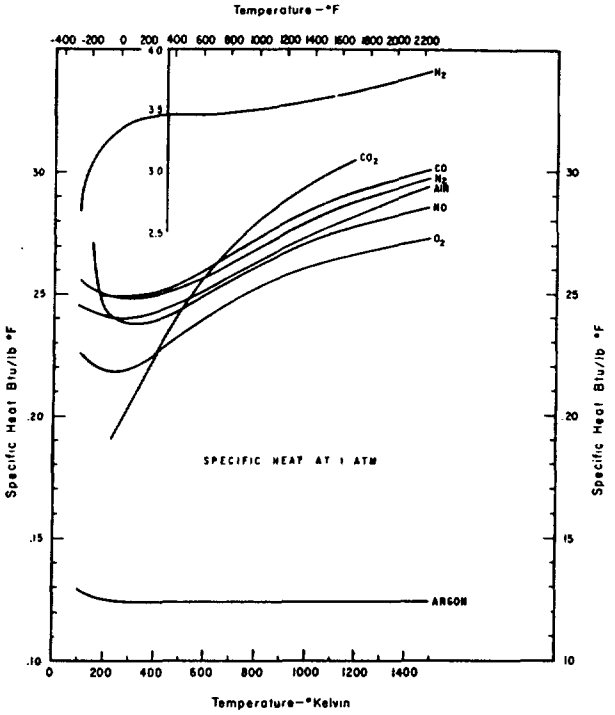


FIGURE 2—Specific of eight gases at atmospheric pressure.

The Prandtl number is dimensionless and is equal to cz (2.42) /k. The Prandtl number for hydrogen and several other common gases[2] at various temperatures are shown in Figure 13. The Prandtl number for hydrogen is of comparable magnitude to that of the other gases even though specific heat and thermal conductivity are relatively high. These factors tend to balance out in the Prandtl number relationship.

Process calculations involving mixtures of hydrogen with liquids involve fluid flow for two-phase systems. The method of Chenoweth and Martin[18] is recommended for these problems.

Both viscosity and thermal conductivity are transport properties. These are dependent upon forces between molecules. The energy of interaction between polar molecules is quite different from that of non-polar molecules. Hydrogen has a non-polar molecule.

Recommended methods of determining the properties of hydrogen mixtures for heat transfer and fluid flow are described here. Viscosity and thermal conductivity calculations by different methods are shown. The simplest solutions, which appear to give results suitable for engineering calculations are those of Bromley and Wilke[4] for viscosity and the author's presentation for thermal conductivity.

The density of hydrocarbon vapors is determined from the ideal gas law with an appropriate correction factor, $n = PV/RT$. The correction factor is plotted as a function of the reduced temperature (T/T_c) and reduced pressure (P/P_c).[7] For hydrocarbon mixtures the pseudo-critical temperature and pressure should be used. The average boiling point method[17] is recommended to calculate the pseudo-critical properties.

When gases (H_2,H_2O, H_2S, etc.) are present in a mixture of hydrocarbon vapors, the reduced pressure of the

Properties of Hydrogen Mixtures . . .

hydrocarbon portion should be based upon the effective pressure of $P\sqrt{x_{hc}}$ for the hydrocarbon portion. The correction factor, n, for the other gases should be also determined at an effective pressure equal to the total pressure multiplied by the square root of its mole fraction. The molal volume is then calculated by Amagat's Law.[7]

$$V_m = \frac{RT}{P}(x_{hc}n_{hc} + x_a n_a + \ldots + x_n n_n)$$

Usually the correction factors for gases are equal to 1.0.

The specific heat of hydrogen as a function of pressure and temperature has been presented in a convenient, graphical form[1] (Figure 1).

The effect of pressure upon the specific heat is slight. The temperature effect is unusual. At low pressures the specific heat increases at a decreasing rate and then increases at an increasing rate. At high pressure, the specific heat decreases at a decreasing rate and then increases at an increasing rate. The point of inflection occurs near 500 F.

The specific heat of hydrogen is approximately thirteen times that of the other common gases as shown in Figure 2.[2]

The specific heat of a mixture of gases at low pressure is equal to the sum of the products of the individual weight fractions times the respective specific heats.

$$c_m = x_a c_a + x_b c_b + \ldots x_n c_n \qquad (1)$$

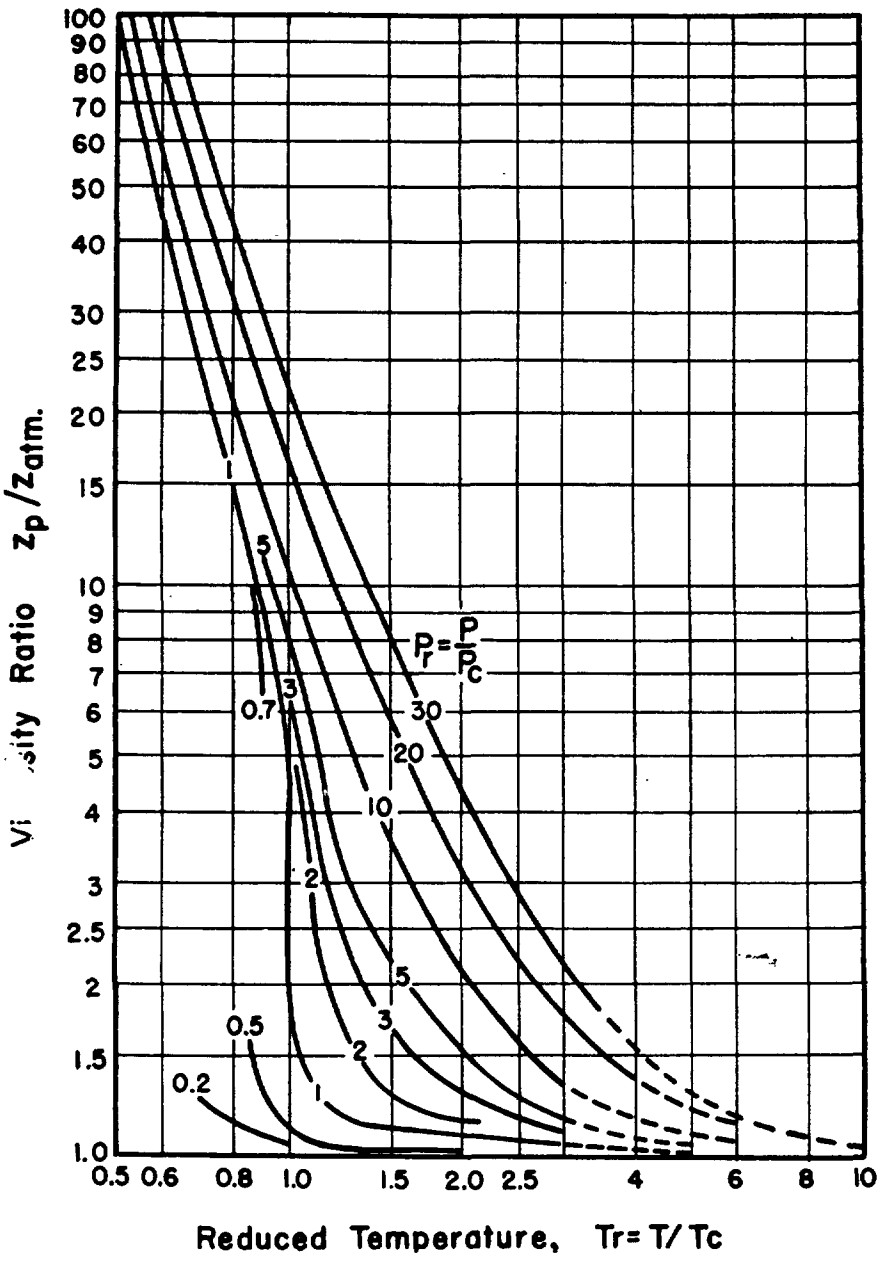


FIGURE 4—Generalized pressure correction to viscosity.

The specific heat of a mixture of gases at high pressure is calculated from enthalpy data. The heat load in the system under consideration should be determined by multiplying the individual weight fractions times the respective enthalpy changes. The specific heat of the mixture is equal to the enthalpy change divided by the temperature change.

$$H = x_a(h_1 - h_3) + x_b(h_1 - h_3) + \ldots + x_n(h_1 - h_3) \qquad (2)$$

$$c_m = \frac{H}{t_1 - t_3} \qquad (3)$$

The viscosity of hydrogen as a function of temperature is shown in Figure 3. The effect of pressure was expected to be small.[1] The recently published data of Hilsenrath & Touloukian[2] shows the effect of pressure on viscosity at 100 atmospheres to be about 1 percent or less for temperatures of 272 F and higher. The viscosity of hydrogen (nitrogen, oxygen, carbon dioxide, and steam) as a function of temperature (—238 to 2192 F) and of pressure (to 100 atmospheres) are given by these authors.[2]

The effect of pressure and temperature upon viscosity has been developed by Uyehara and Watson.[3] A more convenient plot[4] of their data is given in Figure 4. The ratio of viscosity at pressure, P, to the viscosity at one atmosphere, z_p/z_{atm}, as a function of reduced temperature for

TABLE 1
Viscosities of Hydrogen and Nitrogen Under Pressure

Pressure Atmospheres	PSI	VISCOSITY IN CENTIPOISES			
		Temperature 122 F		Temperature 212 F	
		Hydrogen	Nitrogen	Hydrogen	Nitrogen
1	14.7	.00938	.01896	.01030	.02109
50	735	.00952	.01968	.01040	.02159
100	1470	.00963	.02072	.01049	.02250
150	2205	.00973	.02202	.01060	.02351
200	2940	.00983	.02350	.01068	.02464

From Hiroji Iwasaki[5]

various lines of constant reduced pressure is shown.

EXAMPLE—Calculate the viscosity of hydrogen at minus 234 F and 1470 psia. Given viscosity at this temperature and at one atmosphere is 0.0481 centipoise. Critical temperature is minus 400 F. Critical pressure is 175 psia.

$$T_r = \left(\frac{-234+460}{-400+460}\right) = \frac{226}{60} = 3.77$$

$$P_r = \frac{1470}{175} = 8.4$$

From Figure 4 the viscosity ratio is 1.15

$$z_p = 1.15 \times 0.0481 = 0.0553 \text{ centipoise}$$

The viscosity shown by Hilsenrath and Touloukian[2] is 0.0534 centipoise.

The viscosity of hydrogen and nitrogen mixtures at moderate temperatures (122 and 212 F) and at pressures up to 200 atmospheres are presented[5] in Figures 5 and 6. The data for the pure gases (Table 1) by the same author are in close agreement with Hilsenrath.[2] Iwasaki[5] presents a method for calculating the viscosity of these mixtures.

The viscosities[6] of binary mixtures of hydrogen with ethane, carbon monoxide, oxygen, nitrous oxide, methane, propane and nitrogen as determined by experiment and calculation are given in Table 2. It is of particular interest to note that the viscosity of many of these mixtures is greater than the viscosity of either of the components!

TABLE 2
Viscosities of Binary Mixtures
Viscosity in Centipoises

Mol. % H_2 / °F	VISCOSITY H_2-C_2H_6					
	0.0	45.00	85.15	100.0		
68 EX	.00909	.00987	.00993	.00876	.....	.....
CG	.00909	.00986	.01005	.00876	.....	.....
212 EX	.01142	.01208	.01189	.01033	.....	.....
CG	.01139	.01213	.01197	.01021	.....	.....
392 EX	.01409	.01467	.01412	.01213	.....	.....
CG	.01401	.01469	.01411	.01185	.....	.....
482 EX	.01526	.01583	.01511	.01296	.....	.....
CG	.01522	.01588	.01513	.01265	.....	.....
% H_2 / °F.	VISCOSITY H_2-CO_2					
	0.0	19.93	41.29	78.50	100.0	
81 EX*	.01493	.01501	.01506	.01370	.00891	.....
CG*	.01493	.01507	.01508	.01372	.00889	.....
CD*	.01493	.01509	.01512	.01379	.00889	.....
260 EX	.01944	.01945	.01933	.01713	.01081	.....
CG	.01920	.01926	.01913	.01698	.01065	.....
CD	.01920	.01928	.01918	.01703	.01065	.....
440 EX	.02353	.02358	.02321	.02026	.01256	.....
CG	.02301	.02302	.02275	.01990	.01228	.....
CD	.02301	.02303	.02280	.01998	.01228	.....
530 EX	.02556	.02542	.02506	.02173	.01341	.....
CG	.02479	.02478	.02445	.02130	.01308	.....
CD	.02479	.02479	.02450	.02137	.01308	.....
Mol. % H_2 / °F.	VISCOSITY H_2-O_2					
	0.0	18.35	39.45	60.30	78.08	100.0
81	.02057	.02019	.01925	.01784	.01494	.00889
	.02064	.02021	.01934	.01774	.01524	.00889
	.02064	.02024	.01939	.01782	.01531	.00889
260	.02568	.02507	.02381	.02192	.01858	.01087
	.02567	.02506	.02388	.02178	.01857	.01065
	.02567	.02509	.02394	.02186	.01865	.01065
440	.03017	.02950	.02790	.02556	.02158	.01259
	.03015	.02940	.02795	.02541	.02158	.01228
	.03015	.02943	.02802	.02551	.02168	.01228
530	.03220	.03147	.02978	.02733	.02288	.01381
	.03224	.03140	.02986	.02714	.02302	.01308
	.03224	.03146	.02993	.02721	.02313	.01308

Mol. % H_2 / °F.	VISCOSITY H_2-N_2O					
	0.0	39.89	59.61	78.57	100.0	
81 EX	.01488	.01481	.01451	.01348	.00891	.....
CG	.01489	.01509	.01483	.01376	.00889	.....
260 EX	.01943	.01907	.01849	.01684	.01081	.....
CG	.01936	.01932	.01876	.01710	.01065	.....
440 EX	.02355	.02292	.02206	.01990	.01256	.....
CG	.02338	.02311	.02229	.02009	.01228	.....
530 EX	.02555	.02477	.02376	.02137	.01341	.....
CG	.02525	.02489	.02392	.02150	.01308	.....
Mol. % H_2 / °F.	VISCOSITY H_2-CH_4					
	0.0	28.08	48.55	60.22	92.23	100.0
68 EX	.01087	.01099	.01098	.01086	.00955	.00876
CG	.01092	.01102	.01096	.01083	.00952	.00876
CD	.01092	01105	.01101	.01088	.00955	.00876
212 EX	.01331	.01337	.01328	.01306	.01132	.01033
CG	.01327	.01329	.01313	.01291	.01115	.01021
CD	.01327	.01333	.01318	.01297	.01119	.01021
392 EX	.01603	.01602	.01587	.01551	.01338	.01213
CG	.01588	.01583	.01557	.01525	.01300	.01185
CD	.01588	.01585	.01561	.01531	.01303	.01185
482 EX	.01725	.01718	.01699	.01662	.01423	.01296
CG	.01709	.01701	.01670	.01634	.01389	.01265
CD	.01709	.01704	.01675	.01641	.01393	.01265
Mol. % H_2 / °F.	VISCOSITY H_2-C_3H_8					
	0.0	37.04	78.82	92.25	100.0	
81 EX	.00817	.00874	.00985	.00970	.00891	.....
CG	.00819	.00892	.00995	.00980	.00889	.....
260 EX	.01070	.01130	.01233	.01194	.01081	.....
CG	.01074	.01152	.01241	.01194	.01065	.....
440 EX	.01308	.01366	.01459	.01392	.01256	.....
CG	.01309	.01390	.01462	.01389	.01228	.....
530 EX	.01422	.01478	.01566	.01435	.01347	.....
CG	.01418	.01499	.01566	.01482	.01308	.....
Mol. % H_2 / °F.	VISCOSITY H_2-N_2					
	0.0	25.00	50.00	75.00	100.0	.....
—312 EX	.00544	.00540	.00524	.00493	.00362	.....
CG	.00564	.00564	.00552	.00508	.00356	.....
66 EX	.01746	.01700	.01609	.01396	.00882	.....
CG	.01744	.01699	.01605	.01393	.00874	.....

From Hirschfelder, Bird and Spotz[6].
* EX—Experimental data; CG—Calculated using a geometric mean E; CD—Calculated using an E calculated from diffusion.

Hirschfelder, Bird, and Spotz[6] calculated the viscosities (indicated with "CG" and "CD") by using force constants. The author used the Bromley and Wilke[4] method to calculate the viscosities. The experimental viscosities as reported[6] were used for the pure components. The latter method is much less tedious and gives results of a comparable accuracy.

The Viscosity of a Mixture of gases can be determined by the following equation by Maxwell:[7]

$$z_m = \frac{x_1 z_1 \sqrt{m_1} + x_2 z_2 \sqrt{m_2} \ldots + x_n z_n \sqrt{m_n}}{x_1 \sqrt{m_1} + x_2 \sqrt{m_2} + \ldots + x_n \sqrt{m_n}} \quad (4)$$

In a series of papers[4,8,9] Wilke and others developed a method to determine the viscosity of a gas mixture. These equations are:

$$z_m = \frac{z_1}{1 + \frac{x_2}{x_1}\phi_{12}} + \frac{z_2}{1 + \frac{x_1}{x_2}\phi_{21}} \quad (5)$$

$$\phi_{12} = \frac{\left[1 + \left(\frac{z_1}{z_2}\right)^{1/2}\left(\frac{m_2}{m_1}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}}\left[1 + \frac{m_1}{m_2}\right]^{1/2}} \quad (6)$$

$$\phi_{21} = \frac{\left[1 + \left(\frac{z_2}{z_1}\right)^{1/2}\left(\frac{m_1}{m_2}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}}\left[1 + \frac{m_2}{m_1}\right]^{1/2}} \quad (7)$$

Generalized plots of Function ϕ for gas mixtures are

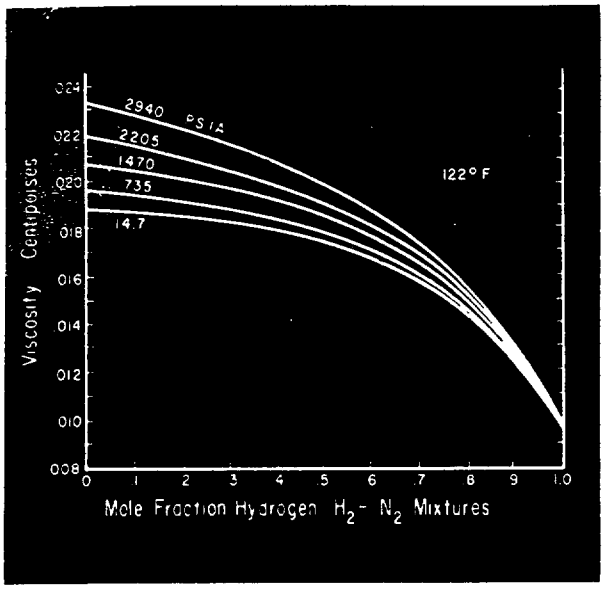


FIGURE 5—Viscosity of hydrogen-nitrogen mixtures at 122 F.

shown in Figures 7 and 8.

EXAMPLE—Calculate the viscosity of a 59.61 percent hydrogen-nitrous oxide mixture at 81 F.

	Hydrogen	Nitrous Oxide
Viscosity (centipoises) at 81 F.	0.00891	0.01488
Molecular weight	2.016	44.02

SOLUTION—by the Maxwell equation (4)

$$z_m = \frac{(0.5961)(0.00891)\sqrt{2.016} + (0.4039)(0.01488)\sqrt{44.02}}{0.5961\sqrt{2.016} + 0.4039\sqrt{44.02}}$$

$$= 0.01345 \text{ centipoise.}$$

Experimental result[9] is 0.1451 centipoise.
Calculated result is 7.3 percent lower.

SOLUTION—by the Bromley and Wilke method

$$\frac{m_1}{m_2} = \frac{2.016}{44.02} = 0.0459$$

$$\frac{z_1}{z_2} = \frac{.00891}{.01481} = 0.600$$

From Figure 4 $\phi_{12} = 2.5$

$$\frac{m_2}{m_1} = \frac{44.02}{2.016} = 21.8$$

$$\frac{z_2}{z_1} = \frac{.01481}{.00891} = 1.67$$

From Figure 8 $\phi_{21} = 0.19$

By equation (5)

$$z_m = \frac{.00891}{1 + \frac{.4039}{.5961}(2.5)} + \frac{.01488}{1 + \frac{.5961}{.4039}(0.19)} = .01494 \text{ centipoise.}$$

Calculated result is 3.0 percent higher than experimental result.

Hirschfelder, Curtiss and Bird[10] present the development of a rigorous kinetic theory for monatomic gases. The final result of this development is the expression of the various transport coefficients in terms of a set of integrals.

These depend upon the force law which is assumed for the molecular interaction. The integrals are evaluated and the calculations are made of the transport coefficients—including viscosity and thermal conductivity—for spherically symmetrical potential functions. The most useful potential function is the Lennard-Jones (6-12) potential. The transport phenomena of molecules with spherically symmetric force fields are well understood. For polar gases and for molecules, which lack spherical symmetry, more work must be done.

The coefficient of viscosity of a pure gas is given by

$$z = \frac{266.93\sqrt{mK}}{D^2 W 10^4} \quad (8)$$

The Force Constants for the Lennard-Jones potential are given in Table I-A[10] for various gases. In this article we refer to the collision diameter (in angstroms) as D and the potential parameter (in degrees Kelvin) as E. The appropriate integral, designated as W for viscosity and thermal conductivity calculations is given in Table I-M.[10] It is necessary to determine the Reduced Temperature, T*, to utilize Table I-M.[10]

$$T^* = K/E \quad (9)$$

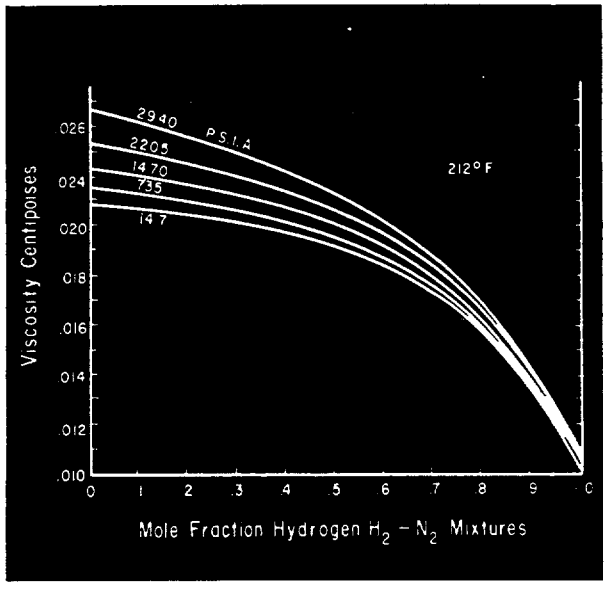


FIGURE 6—Viscosity of hydrogen-nitrogen mixtures at 212 F.

Equation 8.2-19 of the text[10] introduces a correction factor, which varies from zero to 0.8 percent.

EXAMPLE—Calculate the viscosity of methane at 350 F.

$$m = 16.04$$
$$K = 450 \text{ K}$$

From Table I-A[10] the force constants for methane are

$$E = 137 \text{ K and } D = 3.882 \text{ angstroms.}$$
$$T^* = K/E = 450/137 = 3.28$$

From Table I-M[10] $W = 1.016$

By Equation (8)

$$z = \frac{266.93\sqrt{(16.04)(450)}}{(3.882)^2(1.016)(10)^4} = 0.0148 \text{ centipoise}$$

The viscosity of a binary mixture can be determined from

$$z_{12} = \frac{266.93\sqrt{2m_1m_2K/(m_1 + m_2)}}{10^4 D_{12}^2 W_{12}} \quad (10)$$

where z_{12} is the viscosity of a hypothetical substance of molecular weight $2m_1m_2/(m_1 + m_2)$ and the molecules interact according to a potential curve specified by the

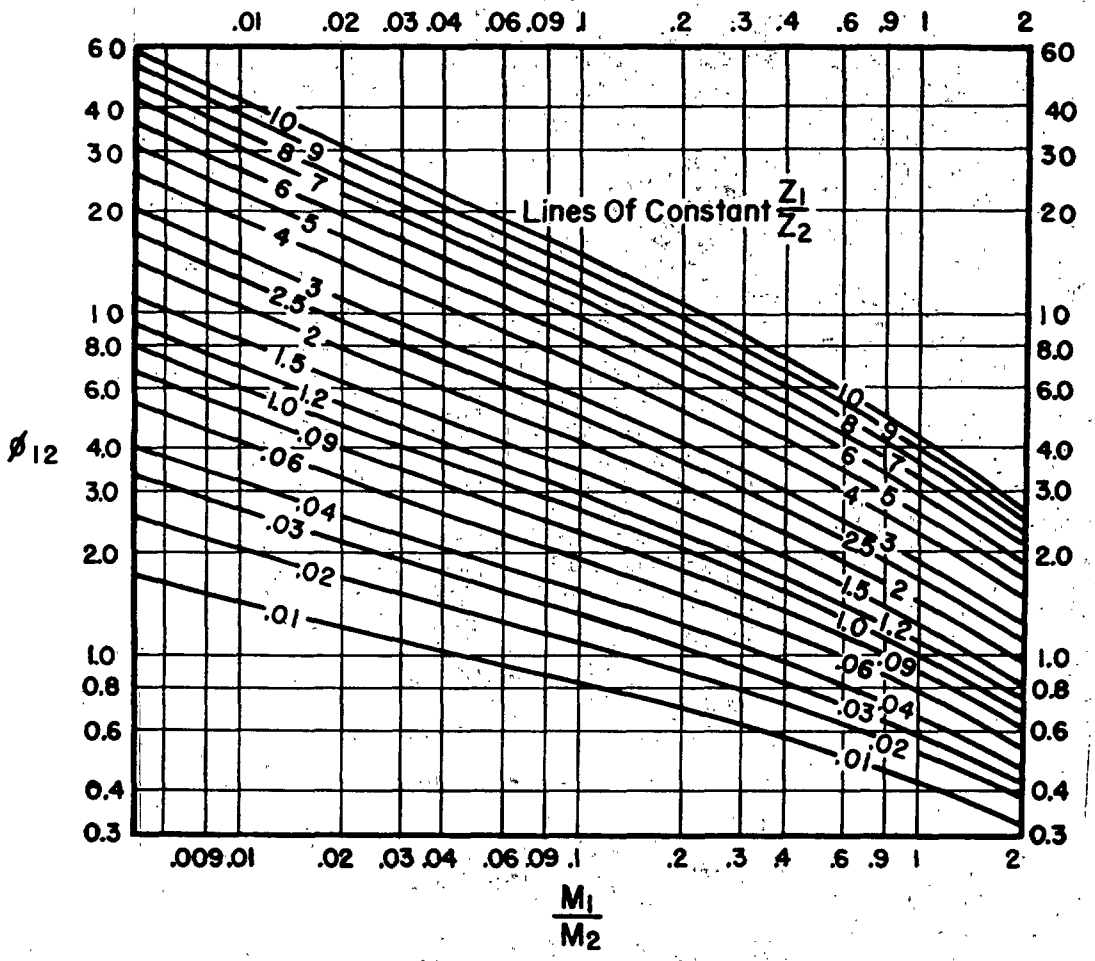


FIGURE 7—Generalized plot of function ϕ for gas mixture viscosities.

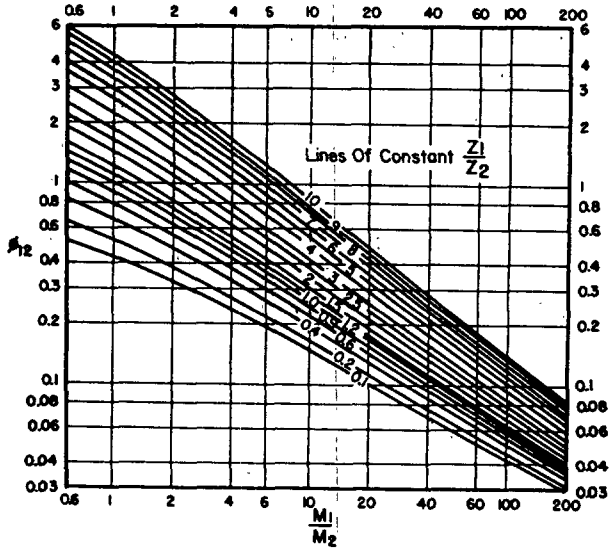


FIGURE 8—Generalized plot of function ϕ for gas mixture viscosities.

interaction parameters D_{12} and W_{12}.

EXAMPLE—Calculate the viscosity of a mixture of 23.37 mole percent nitrogen and 76.63 mole percent CO at 226.9 C.

SOLUTION: at 226.9 C, K = 500.1 Kelvin.

Gas	(Angstroms)	(Kelvin)	Source	Mol. Wt.
N_1	$D_1 = 3.681$*	$E_1 = 91.5$*	Table I-A[20]	28.02
CO	$D_2 = 3.706$	$E_2 = 88.0$	Table I-A[20]	28.01
N_2-CO	$D_{12} = 3.694$	$E_{12} = 89.7$	See below	

$$D_{12} = 0.5\ (3.681 + 3.706) = 3.694 \text{ angstroms}$$

$$E_{12} = \sqrt{(9.15)\ (88.0)} = 89.7 \text{ K}$$

$T^* = K/E$	W (from Table I-M[20])
$T_1^* = 500.1/91.5 = 5.446$	0.9127
$T_2^* = 500.1/88.0 = 5.683$	0.9060
$T_{12}^* = 500.1/89.7 = 5.557$	0.9093

From Table I-N[20] $A_{12}^* = 1.102$

* Data used in "Molecular Theory of Gases and Liquids"[19] page 569, although these values are recommended for use below 300 Kelvin.

Equation (8)

$$Z_1 = \frac{266.93\ \sqrt{(28.02)\ (500.1)}}{(3.681)^2\ (0.9127)\ 10^5} = 0.02555 \text{ centipoise}$$

$$Z_2 = \frac{266.93\ \sqrt{(28.01)\ (500.1)}}{(3.706)^2\ (0.9060)\ 10^5} = 0.02539 \text{ centipoise}$$

Equation (10)

$$Z_{12} = \frac{266.93\ \sqrt{(28.02)\ (28.01)\ (500.1)/(28.02 + 28.01)}}{(3.694)^2\ (0.9093)\ 10^5} = .02546 \text{ centipoise}$$

The viscosity of the binary mixture is given by Equation (11).

$$\frac{1}{(z_{mix})_1} = \frac{X_s + Y_s}{1 + Z_s} = X\left[\frac{1 + (Y_s/X_s)}{1 + Z_s}\right] \qquad (11)$$

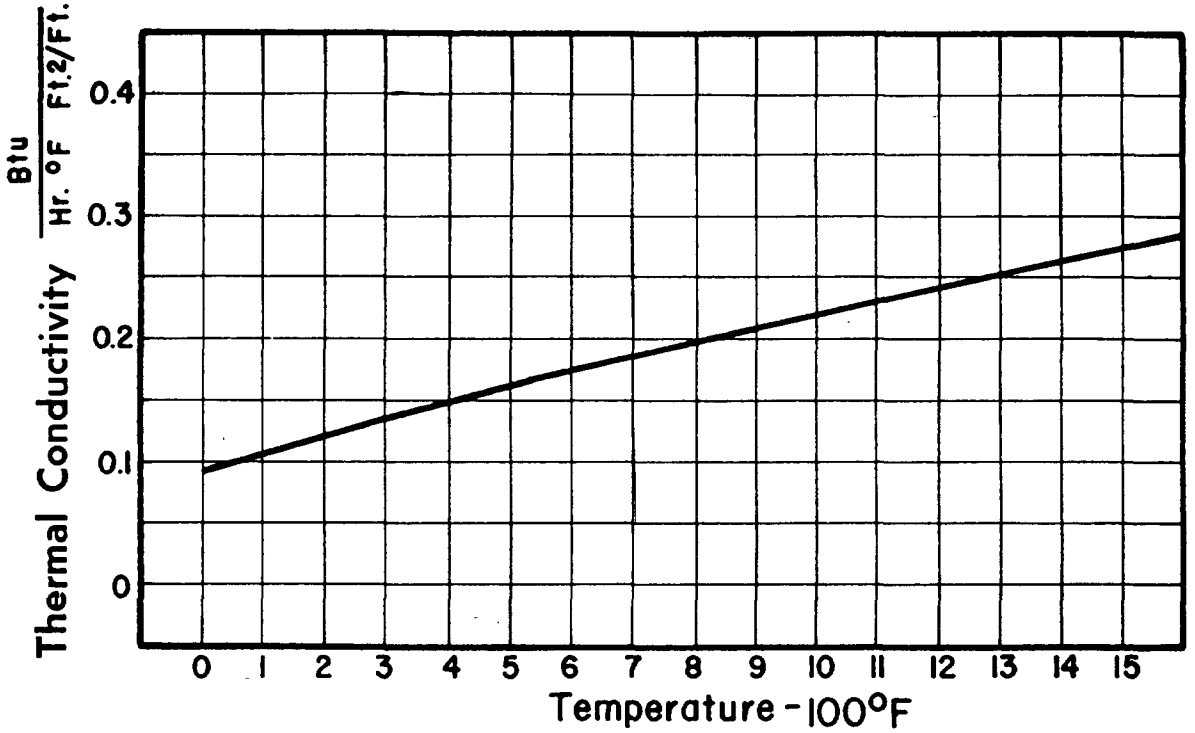


FIGURE 9—Thermal conductivity of hydrogen.

TABLE 3
Thermal Conductivity
Thermal Conductivity in BTU/hr. sq. ft. °F./ft

	PRESSURE—Pounds/Square Inch Absolute						
	°F	14.22	1422	2844	4266	5688	7110
Hydrogen	59	.1014	.1042	.1080	.1103	.1111	1116
	212	.1222	.1236	.1262	.1274	.1283	.1288
	392	.1458	.1467	.1486	.1496	.1503	.1504
	572	.1693	.1700	.1716	.1726	.1729	.1731
Nitrogen	59	.0145	.0163	.0211	.0251	.0273	.0308
	212	.0178	.0184	.0219	.0254	.0272	.0306
	392	.0213	.0217	.0238	.0263	.0278	.0307
	572	.0249	.0250	.0265	.0286	.0298	.0323
Air	68	.0149	.0161	.0220	.0262	.0292	....
	212	.0177	.0178	.0217	.0249	.0271	....
	356	.0209	.0211	.0236	.0443	.0281	....
ane	58	.0194	.0261	.0379	.0437	.0473	.0487
	212	.0262	.0284	.0358	.0404	.0432	.0442
	392	.0344	.0350	.0405	.0423	.0445	.0451
Carbon Dioxide	127	.0111	.0323	.0485	....	....	....
	185	.0126	....	.0374	.0460	....	....
	212	.0135	.0196	.0353	.0444	....	....
	302	.0161	.0178	.0283	.0370	....	....
	392	.0185	.0191	.0259	.0335	....	....

From Stolyanov, Ipatiev and Teodorovich[11].

$$X_s = \frac{x_1^2}{(z_1)_1} + \frac{2x_1x_2}{(z_{12})_1} + \frac{x_2^2}{(z_2)_1} \qquad (11A)$$

$$Y_s = 0.6\,(A_{12}^*)\left\{\frac{x_1^2}{(z_1)_1}\left(\frac{m_1}{m_2}\right) + \frac{2x_1x_2}{(z_{12})_1}\left(\frac{(m_1+m_2)^2}{4m_1m_2}\right)\left(\frac{(z_{12})_1^2}{(z_1)_1(z_2)_1}\right) + \frac{x_2^2}{(z_2)_1}\left(\frac{m_2}{m_1}\right)\right\} \qquad (11B)$$

$$Z_s = 0.6\,(A_{12}^*)\left\{x_1^2\left(\frac{m_1}{m_2}\right) + 2x_1x_2\left[\left(\frac{(m_1+m_2)^2}{4m_1m_2}\right)\left(\frac{(z_{12})_1}{(z_1)_1}\right) + \frac{(z_{12})_1}{(z_{12})_1} - 1\right)\right] + x_2^2\frac{m_2}{m_1} \qquad (11C)$$

Solving Equation (11), using data from the proceeding example, gives the concentration dependence of the viscosity of N_2 — CO mixtures at 226.9 C

$$Z_{mix} = \frac{16613x_1^2 + 33214x_1x_2 + 16611x_2^2}{(10^5)\,(6.5023x_1^2 + 13.0455x_1x_2 + 6.5423x_2^2)}$$

For $x_1 = 0.2337$ $x_2 = 0.7763$

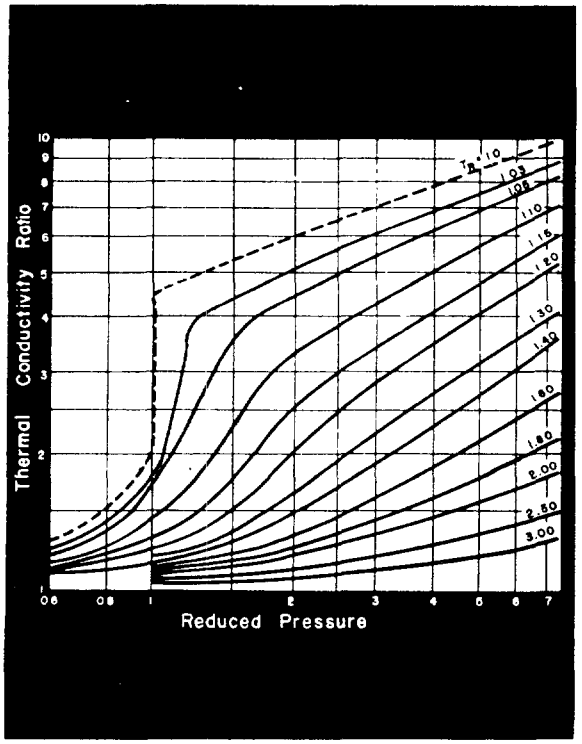
$Z_{mix} = .02542$ centipoise

Experimental data give 0.02550 centipoise.

Thermal conductivity of hydrogen as a function of temperature has been presented in a convenient form[1] and is reproduced in Figure 9. The effect of pressure was expected to be small and recently published[11] Russian data, extending to some 485 atmospheres, confirm this as shown in Table 3. There is a 10 percent increase in conductivity at 59 F and a 2.2 percent increase at 572 F. The thermal conductivity of nitrogen, air, methane, and carbon dioxide under pressure were also investigated and the results are presented. Pressure greatly effects the thermal conductivity of these gases.

The effect of pressure and temperature upon thermal conductivity has been developed by Lenoir, Junk, and Comings.[12-4] The ratio of thermal conductivity at pressure, P, to the thermal conductivity at one atmosphere, k_p/k_{atm}, as a function of reduced pressure for various lines of constant reduced temperature is shown in Figure 11. The Russian data extend considerably beyond the range of this figure. (eg. The reduced pressure of hydrogen at the highest tabulated value is 40, while the curve extends to a reduced pressure of 7.)

The thermal conductivities of gaseous mixtures con-



Recent work indicates that this figure predicts values approximately 40 percent too high for ethane and 60 percent too high for propane in some regions. The behavior of the more complex organic compounds is more complicated than is shown by this figure.

FIGURE 10—Generalized pressure correction to thermal conductivity.

taining hydrogen are presented[13] in Table 4.

Lindsay and Bromley[14] developed the following relationship for the thermal conductivity of mixtures.

$$k_m = \frac{k_1}{1 + A_{12}\frac{x_2}{x_1}} + \frac{k_2}{1 + A_{21}\frac{x_1}{x_2}} \qquad (12)$$

$$A_{12} = 0.25\left\{1 + \left[\frac{z_1}{z_2}\left(\frac{m_2}{m_1}\right)^{0.75}\frac{\left(1+\frac{S_1}{T}\right)}{\left(1+\frac{S_2}{T}\right)}\right]^{0.5}\right\}^2\frac{\left(1+\frac{S_{12}}{T}\right)}{\left(1+\frac{S_1}{T}\right)} \qquad (13)$$

The same expression gives A_{21} when the subscripts are interchanged.

$S = 1.5\,T_B$

$S = 142$ Kelvin for hydrogen, deuterium, helium

$S_{12} = \sqrt{S_1 S_2}$ for nonpolar mixtures

$S_{12} = 0.733\sqrt{S_1 S_2}$ for polar mixtures with steam or ammonia

Brokaw[13] developed a simpler relationship for the thermal conductivity of a nonpolar gas mixture.

$$k_m = a\,k_{SM} + (1 - a)\,k_{RM} \qquad (14)$$

$$k_{SM} = x_1 k_1 + x_2 k_2 \qquad (15)$$

$$\frac{1}{k_{RM}} = \frac{x_1}{k_1} + \frac{x_2}{k_2} \qquad (16)$$

The dimensionless factor, a, is presented in Figure 11.

The author has developed an extremely simple equation

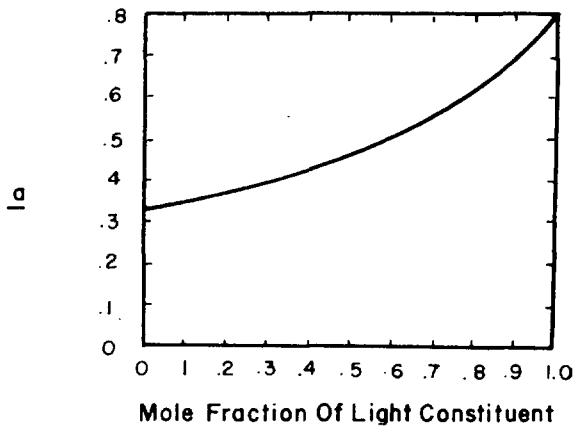


FIGURE 11—Dimensionless factor, a.

for the thermal conductivity of a gas mixture containing hydrogen.

$$k_m = f\left[\left(\frac{x_1 + X_1}{2}\right)k_1 + \left(\frac{x_2 + X_2}{2}\right)k_2\right] \qquad (17)$$

The dimensionless factor, f, is presented in Figure 12. This empirical relationship represents all the data in Table 4 with an accuracy of 3.3 percent and a maximum deviation of 8.6 percent.

Hirschfelder, Curtiss, and Bird[10] present the following methods for determining the thermal conductivity of a

TABLE 4

Thermal Conductivities of Binary Mixtures, Containing Hydrogen

Gas Pair	Literature Reference	Temperature °F	Mole Fraction Hydrogen	Thermal Conductivity Btu/Hr. Sq. Ft. °F./Ft.
H_2-CO_2	18	32	0	0.00871
			0.142	.01380
			0.355	.02420
			0.50	.03265
			0.75	.0549
			0.901	.0762
			1.00	.0978
H_2-N_2	18	32	0.0	0.01331
			0.159	.01936
			0.390	.03073
			0.652	.0469
			0.803	.06215
			1.00	.0978
H_2-N_2O	18	32	0.0	0.0092
			0.209	.01718
			0.386	.02590
			0.599	.0411
			0.812	.0658
			1.00	.0978
H_2-CO	18	32	0.0	0.01283
			0.163	.01936
			0.272	.02492
			0.566	.0438
			0.634	.0506
			0.794	.0653
			1.00	.0978
H_2-C_2H_4	18	77	0.0	0.01277
			0.1698	.02082
			0.3140	.02778
			0.5137	.0409
			0.6110	.04985
			0.8649	.0796
			1.00	.1058
H_2-CO_2	18	77	0.0	0.00987
			0.047	.01072
			0.193	.01833
			0.496	.0366
			0.9059	.0847
			0.9638	.0973
			1.00	.1058
H_2-CO_2	18	32	0.0	0.00821
			0.1701	.0147
			0.3693	.02503
			0.6068	.0417
			0.8346	.0677
			1.00	.1058

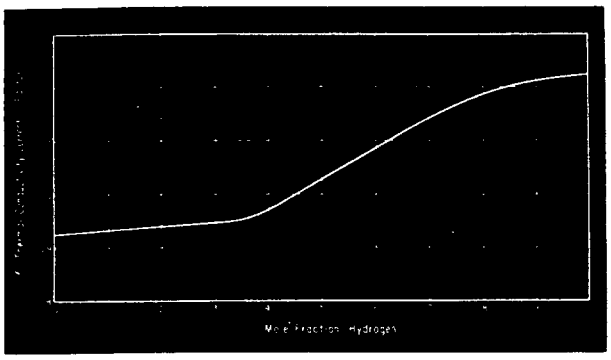


FIGURE 12—Dimensionless factor, f.

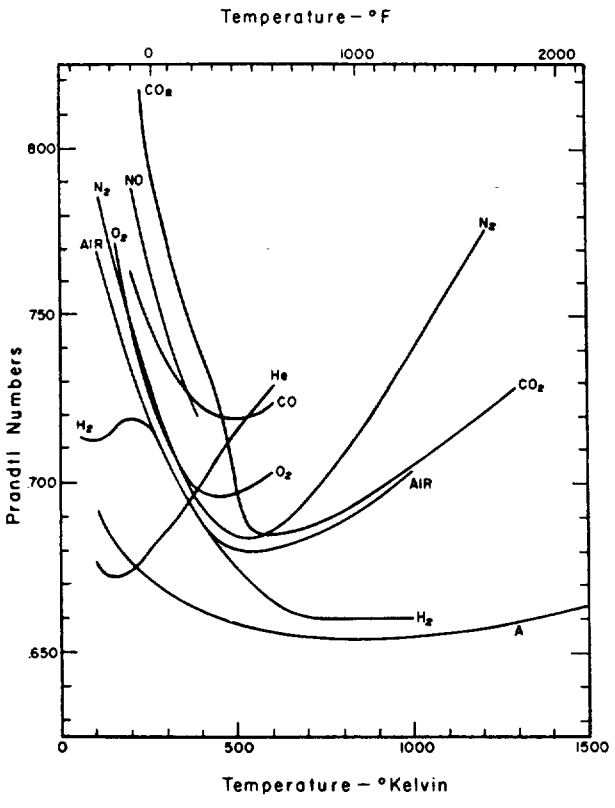


FIGURE 13—Prandtl number for nine gasses.

gas and of a gaseous mixture.

$$k = \frac{0.0482\sqrt{K/m}}{D^2 W}\left[\frac{4}{15}\cdot\frac{C}{R}+\frac{3}{5}\right] \qquad (18)$$

$\left[\frac{4}{15}\cdot\frac{C}{R}+\frac{3}{5}\right]$ is a factor for the transfer of energy between translational and internal degrees of freedom. C, the heat capacity per mole, is equal to 3R/2 for monatomic gases. Thus, the factor reduces to 1.0 for monatomic gases (He, Ne, A, Kr, Xe.)

A higher approximation introduces correction factors to increase the accuracy of the calculation. These factors vary from plus 1.0001 to 1.0125 and are ignored in this presentation. Refer to equation 8.2—32 of the text.[10]

Hirschfelder[10] presents the ratios of calculated to experimental conductivities as shown in the Tables 8.4—10[10] and 8.4—11.[10] Also tabulated are the factors for the transfer of energy.

EXAMPLE—Calculate the thermal conductivity of hydrogen at 32 F.

Use Equation (18).

$K = 273.16$ Kelvin $\quad m = 2.016$

From Table I-A[10] $D = 2.968$ angstroms $\quad E = 33.3$ Kelvin

From Table 8.4-10 and 8.4-11[10] $\left[\frac{4C}{15R}+\frac{3}{5}\right] = 1.255$

$T^* = K/E = 273.16/33.3 = 8.203$

From Table I-M[10] $W = 0.8506$

$$k = \frac{0.0482\sqrt{273.16/2.061}}{(2.968)^2(0.8506)}(1.255) = 0.0939 \text{ Btu/hrs. sq. ft. F/ft.}$$

The thermal conductivity of a mixture is determined from equation

$$k_{12} = \frac{0.0482\sqrt{K(m_1+m_2)/2m_1m_2}}{D_{12}^2 W_{12}} \qquad (19)$$

where k_{12} is the thermal conductivity of a hypothetical substance of molecular weight $2m_1m_2/(m_1+m_2)$ and the molecules interact according to the potential curve specified by the interaction parameters D_{12} and W_{12}. (Refer to example for viscosity of a mixture for methods of determining D_{12} and W_{12}.)

In terms of this quantity and the thermal conductivities of the pure components, the thermal conductivity of a mixture of monatomic gases may be written as

$$\frac{1}{(K_{mix})_1} = \frac{X_k + Y_k}{1+Z_k} \qquad (20)$$

There is at present no rigorous method for calculating the thermal conductivity of mixtures of polyatomic gases. However, an empirical method is suggested by Hirschfelder, et al.[10] First, calculate for the mixture the quantity given by the above Equation (19). The result is denoted by k_{mon}. If the experimental values of k for the pure gases are known, then for each of the components compute the ratio . . .

$$r = \frac{k_i \text{ expt}}{k_{i\ mon}} \qquad (21)$$

An empirical expression for the mixture is . . .

$$k_{mix} = k_{mon}(x_1r_1 + x_2r_2) \qquad (22)$$

$$X_k = \frac{x_1^2}{(k_1)_1} + \frac{2x_1x_2}{(k_{12})_1} + \frac{x_2^2}{(k_2)_1} \qquad (20A)$$

$$Y_k = \frac{x_1^2}{(k_1)_1}U^{(1)} + \frac{2x_1x_2}{(k_{12})_1}U^{(y)} + \frac{x_2^2}{(k_2)_1}U^{(2)} \qquad (20B)$$

$$Z_k = x_1^2U^{(1)} + 2x_1x_2U^{(z)} + x_2^2U^{(2)} \qquad (20C)$$

$$U^{(1)} = \frac{4}{15}A_{12}^* - \frac{1}{12}\left(\frac{12}{5}B_{12}^* + 1\right)\frac{m_1}{m_2} + \frac{1}{2}\frac{(m_1-m_2)^2}{m_1m_2} \qquad (20D)$$

$$U^{(2)} = \frac{4}{15}A_{12}^* - \frac{1}{12}\left(\frac{12}{5}B_{12}^* + 1\right)\frac{m_2}{m_1} + \frac{1}{2}\frac{(m_1-m_2)^2}{m_1m_2} \qquad (20E)$$

$$U^{(y)} = \frac{4}{15}A_{12}^*\left[\frac{(m_1+m_2)^2}{4m_1m_2}\right]\frac{(k_{12})_1^2}{(k_1)_1(k_2)_1} - \frac{1}{12}\left(\frac{12}{5}B_{12}^* + 1\right) - \frac{5}{32}A_{12}^*\left(\frac{12}{5}B_{12}^* - 5\right)\frac{(m_1-m_2)^2}{m_1m_2} \qquad (20F)$$

$$U^{(z)} = \frac{4}{15}A_{12}^*\left[\left(\frac{(m_1+m_2)^2}{4m_1m_2}\right)\left(\frac{(k_{12})_1}{(k_1)_1}+\frac{(k_{12})_1}{(k_2)_1}\right) - 1\right] - \frac{1}{12}\left(\frac{12}{5}B_{12}^* + 1\right) \qquad (20G)$$

EXAMPLE—Calculate the thermal conductivity at 77 F. of a 61.1 percent hydrogen-ethylene mixture.

Properties—

$x_1 = 0.611 \quad x_2 = 0.389$

$z_1 = 0.00953 \quad z_2 = 0.0098$

$m_1 = 2.016$ $m_2 = 28.05$

$T_{B1} = 37$ Rankin $T_{B2} = 305$ Rankin

$S_1 = 1.5 \times 37 = 55.5$ $S_2 = 1.5 \times 305 = 457$

$k_1 = 0.1058$ $k_2 = .01277$

Solution by Lindsay and Bromley method.

By Equation (13)

$$A_{12} = 0.25\left\{1+\left[\frac{.00953}{.0098}\left(\frac{28.05}{2.016}\right)^{0.75}\frac{\left(1+\frac{55.5}{537}\right)}{\left(1+\frac{457}{537}\right)}\right]^{0.5}\right\}^2 \frac{\left(1+\frac{\sqrt{(55.5)(457)}}{537}\right)}{\left(1+\frac{55.5}{537}\right)}$$

$A_{12} = 2.72$

$$A_{21} = 0.25\left\{1+\left[\frac{.0098}{.00953}\left(\frac{2.016}{28.05}\right)^{0.75}\frac{\left(1+\frac{457}{537}\right)}{\left(1+\frac{55.5}{537}\right)}\right]^{0.5}\right\}^2 \frac{\left(1+\frac{\sqrt{(457)(55.5)}}{537}\right)}{\left(1+\frac{457}{537}\right)}$$

$A_{21} = 0.388$

By Equation (12)

$$k_m = \frac{0.1058}{1+2.72\left(\frac{0.389}{0.611}\right)} + \frac{0.01277}{1+0.388\left(\frac{0.611}{0.389}\right)} = .0465$$

Solution by the Brokaw Method.

By Equation (15)

$k_{SM} = (0.611)(0.1058) + (.389)(0.01277) = .0695$

By Equation (16)

$$\frac{1}{k_{RM}} = \frac{0.611}{0.1058} + \frac{0.389}{0.01277} = 36.28$$

$k_{RM} = .0276$

From Figure 11, "a" = 0.50

By Equation (14)

$k_m = 0.50 \times .0695 + (1 - 0.50)\ .0276 = .0496$

By the author's method—Equation (17)

From Figure 12 $f = 1.092$

$$x_1 = \frac{0.611 \times 2.016}{(0.611 \times 2.016) + (0.389 \times 28.05)} = 0.101$$

$x_2 = 1.0 - 0.101 = 0.899$

$$k_m = 1.092\left[\left(\frac{0.611+0.101}{2}\right)(0.1058) + \left(\frac{0.389+.899}{2}\right)(.01277)\right] = 0.0500 \text{ Btu/hr. - sq. ft. - F/ft.}$$

Thermal conductivity of mixture.

Table 4	0.04985
Equation (12)	0.0465
Equation (14)	0.0496
Equation (17)	0.0500

NOMENCLATURE

A — dimensionless constant (Lindsay & Bromley equation)
A* — the quantity A* for calculating the transport coefficients of mixtures for the Lennard-Jones (6-12) potential
a — dimensionless factor (Brokaw equation)
B* — the quantity B* for calculating the transport coefficients of mixtures for the Lennard-Jones (6-12) potential
C — specific heat at constant volume, calories per gram mole per degree Kelvin
c — specific heat at constant pressure—Btu/lb. F.
D — collision diameter in angstroms
E — potential parameter in degrees Kelvin
f — dimensionless factor (author's equation)
H — enthalpy change—Btu
h — enthalpy—Btu/lb.
K — temperature—degrees Kelvin
k — thermal conductivity—Btu/hr. sq. ft. F./ft.
m — molecular weight
P — pressure—lb./sq. in. absolute
R — gas constant, calories/degrees Kelvin-gram mole or lb./sq. in.-cu. ft./mole per degree Rankin
S — Sutherland constant, degrees Rankin
T — temperature—degrees Rankin
T* — reduced temperature—dimensionless ($T^* = K/E$)
t — temperature—degrees Fahrenheit
V — molal volume—cu. ft./mole
W — integral for calculating viscosity and thermal conductivity (as well as other properties) for the Lennard-Jones (6-12) potential. $W = \Omega^{2,2*}$ in "Molecular Theory of Gases and Liquids."[20]
X — weight fraction
x — mole fraction
z — viscosity—centipoises
ϕ — function of molecular weights and viscosities

Subscripts:

a,b,n — components a,b,n
atm — one atmosphere (14.7 lb./sq. in.)
B — boiling point at one atmosphere
c — critical point
hc — hydrocarbon
m — mixture
p — absolute pressure, lb./sq. in.
r — reduced (temperature or pressure)
RM — reciprocal mixing
SM — simple mixing
1,2 — temperatures 1 and 2, or components 1 and 2
12 — interaction of components 1 and 2

LITERATURE CITED

[1] Granet, Irving, Petroleum Refiner, Vol. 33, May, 1954, 205.
[2] Hilsenrath, J., and Y. S. Touloukian, Trans. ASME, Vol. 76, August, 1954, 967.
[3] Uyehara, O. A., and K. M. Watson, Natl. Petroleum News, Vol. 36, R764 (1944).
[4] Bromley, L. A., and C. R. Wilke, Ind. & Eng. Chem., Vol. 43, 1641 (1951).
[5] Iwasaki, Hiroji, Science Reports of the Research Institutes, Tohoku University (Sci. Rep. Ritu, A-Vol. 6, No. 3), Sendai, Japan, June, 1954, Page 296-307.
[6] Hirschfelder, J. O., R. B. Bird and E. L. Spotz, Chem. Rev., 44, 205, (1949).
[7] Maxwell, J. B., Data Book on Hydrocarbons, Van Nostrand Co. (1950).
[8] Buddenberg, J. W., and C. R. Wilke, Ind. & Eng. Chem., Vol. 41, 1345 (1949).
[9] Wilke, C. R., J. Chem. Phys., Vol. 18, 517 (1950).
[10] Hirschfelder, J. O., C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons (1954).
[11] Stolyanov, E. A., V. V. Ipatlev and V. P. Teodorovich, Zhur, Fiz. Khim., Vol. 24, 166-76 (1950).
[12] Lenoir, J. M., W. A. Junk and E. W. Comings, Chem. Eng. Progress, Vol. 49, 539 (1953).
[13] Brokaw, R. S., Ind. & Eng. Chem., Vol. 47, 2398 (1955).
[14] Lindsay, A. L., and L. A. Bromley, Ind. & Eng. Chem., Vol. 42, 1508 (1950).
[15] Ibbs, T. L., and A. A. Hirst, Proc. Roy. Soc. (London), A 123, 134 (1929).
[16] Kornfeld, G., and K. Hilferding, Z. Physick. Chem. Bodenstein-Festband, 792 (1931).
[17] Smith, R. L., and K. M. Watson, Ind. & Eng. Chem., Vol. 29, 1408 (1937).
[18] Chenoweth, J. M., and M. W. Martin, Petroleum Refiner, Volume 34, 151 (1955).
[19] Getman, F. H., and F. Daniels, "Outlines of Physical Chemistry," Seventh Edition, P. 77, Wiley (1943).

Meet the Author

FRANK L. RUBIN has a background of some 15 years with the chemical, petrochemical, petroleum and power industries. Most of that time has been spent in the design of heat-transfer equipment. With Catalytic Construction Company before joining Dowington he served three years as senior job engineer with special emphasis on heat-transfer problems. His work was on AEC projects, chemical plants and refineries. He also had been with The Lummus Company, in its Heat Exchanger division, and with Stauffer Chemical Company, assigned to Research division. He is a registered professional engineer in Pennsylvania and New York. He holds a B.A. degree from Brooklyn College, a chemical engineering degree from Cooper Union School of Engineering, and has completed graduate studies at The Polytechnic Institute of Brooklyn.

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FACTORS INFLUENCING THE PERFORMANCE OF INTERNAL INSULATING LININGS IN PRESSURE EQUIPMENT

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I. INTRODUCTION

The successful use of internal insulation linings in pressure vessels and pressure piping in recent years has played an important part in the practical application of new processes involving increased combinations of pressure, temperature and size. Present indications are for an increasing and more exacting need for such linings. It is the purpose of this paper to outline factors which should be considered toward assuring satisfactory performance of particular linings. These are presented from the point of view of the designer and user as associated with the experience of the authors' company with the primary objective of promoting discussion and interchange of backround.

In common with the design of the pressure equipment itself, linings can be effectively designed provided complete knowledge of process requirements not only for normal service but also for start-up, emergency and any other conditions which may exist are considered. Similarly other factors which may affect heat flow and consequently metal temperatures must be evaluated and provided for. Unusual conditions require careful consideration - e.g. sudden depressuring which may dislodge or loosen the insulation or rapid cycles of pressure or temperature which may accelerate its deterioration.

The subject matter has been organized for presentation under the following four basic subjects:

Conductivity of Insulation - which treats the heat transfer aspects of the insulation materials along with effects of environment.

Deterioration in Service - which covers the factors contributing to structural changes, mechanical or chemical effects which result in loss of strength or actual disintegration of the insulation.

Performance in Service - which presents factors, (other than those which affect the properties of the insulation material,) which may influence the operating effectiveness of internal insulation.

Design Considerations - which reviews the engineering problems attendant to the design assumptions, selection of materials and design details.

II. CONDUCTIVITY OF INSULATION

Data on basic conductivity are ordinarily obtained from the manufacturer or literature and represents performance under controlled laboratory conditions at atmospheric pressure and in the presence of air or flue gas. These values may be significantly increased in some services by factors which affect the density of the insulation or the composition and density of the gas in the pores or by the deposition of solid matter within the pores so that laboratory values may not be representative of average installation particularly in the case of insulating concrete. In general

low conductivity is achieved by the creation of many small voids, utilizing the lower conductivity of air and reducing the overall heat flow so that, for each material, conductivity is approximately proporti al to the density. Replacement of the ambient pressure air in the pores of the insulation by a denser or more conductive gas or by solid material raises conductivity.

A. Effect of Internal Pressure and Type of Gas on Conductivity

The literature contains little information of this subject but tests have been made which show a very significant effect of hydrogen on low density insulations. The authors have found the following approach logical and useful for design purposes:

(1) $$k = k_1 + xk_g$$

where k_1 is the evacuated insulation conductivity (no gas in pores) at the operating temperature

x is the degree of porosity of the insulation (fractional per cent)

k_g is the conductivity of the gas in the pores under operating conditions

k is the combined effective conductivity of the insulation and gas at operating conditions

The value of k_g depends on the type of gas and its density and pressure. The authors use the following relation which correlates reasonably well with such data as can be found in the literature.

(2) $$k_g = \frac{C_1(T)^{3/2}}{T + C_2} \times \log_{10} C_3 p \quad (\text{BTU/sq.ft/hr./}^{\circ}\text{F/in})$$

where p is the absolute pressure, psi, T the absolute temperature, $^{\circ}$F, and C_1, C_2 and C_3 are constants for each particular gas. Suggested values of these constants for air and hydrogen are

	C_1	C_2	C_3
Air	.0054	225	38.3
Hydrogen	.0342	169	52.2

Due to its high conductivity compared to air hydrogen can increase the conductivity of low conductivity relatively porous insulations 100% or more.

It is readily apparent from equation (1) that the effect of the gas composition and pressure and temperature has a lesser percentage effect where the material has a higher evacuated conductivity, less porosity or both.

Although the thermal conductivity of mixtures of gases cannot be properly calculated by the ordinary arithmetic mixing rule it is suggested that it be applied when using equation (2) for mixtures of two gases as

$$k_g = \frac{p_1}{p_1 + p_2} k_{g1} + \frac{p_2}{p_1 + p_2} k_{g2}$$

It is doubtful whether the conductivity so calculated would seriously effect the design.

Values of "k", must be obtained by solution of equation (1) using known values of k with air at atmospheric pressure in the pores, the known value of x and "k_g" from equation (2).

The apparent porosity, as reflected by the density of the insulation, is not always the proper value to use for "x" since some pores may be sealed off which would make them insensitive to gas composition and pressure. However it is a safe assumption for design investigation; in addition it is possible that due to operating pressure or after long service these cells may rupture.

B. Effect of Deposition of Solids in Pores

Conductivity will generally be increased by the infiltration of additional material such as coke, tar, corrosion products, catalyst dust etc. No simple evaluation of these effects can be made. Coke deposition in raising the effective conductivity of the insulation should be less where the material has a higher evacuated conductivity, less porosity or both. The exact effect may be quite variable however since the coke deposit may vary widely in its density (probably similar to thermal cracking where coke conductivities from 0.25 to 10 have been reported) and in the manner in which it is laid down. In some cases insulating brick or concrete thoroughly blackened shows little if any increase in density. In services where alternate reaction and regeneration is involved the blackened area will exist only in areas remote from the flow. The authors have not been able to detect any great effect from the coking of insulating concrete in reactor service in analyzing observed metal temperature.

Obviously the effects of gas composition, pressure and solid deposition compete for the same void volume and their separate influences are not directly additive. This should be considered when establishing a design factor for all effects.

III. DETERIORATION IN SERVICE

Many factors may cause deterioration in service so that is is not practicable to fully discuss each at length in this paper. Certain major factors must be considered when choosing materials and design details. They may be listed as:

1. Suitability of materials
2. Application variables

3. Mechanical deterioration
4. Structural deterioration
5. Chemical deterioration
6. Carbon deposition and similar effects
7. Short or long time failure due to overloading

Materials must be selected with proper regard for their temperature stability, inertness to the operating atmosphere, and corrodents which may be present on stream or shut-down.

The importance of careful installation cannot be over-emphasized since many failures can be directly associated with faulty application. The important safety function of insulating linings and maintenance economics warrant the additional care and cost in preparing detailed instructions for the installation and for the adequate supervision and inspection necessary to have these specifications followed.

Mechanical deterioration may take the form of spalling, cracking opening of joints, erosion or failure due to support details or vibration. Spalling is largely associated with thermal shock, either during initial curing or in service. Obviously rapid heating or cooling such as contact of hot surfaces by water sprays should be avoided. Cracking may be the result of shrinkage, thermal stress within the insulation or differential expansion between the insulation and the shell or other metal parts. Concrete linings, because of the low tensile strength of concrete, may be expected to show hair line fissures which open upon cooling down. Without growth these are not significant but under cyclic operation and perhaps under the wedging action of infiltrated solids the cracks may grow and lead to spalling. Opening up of joints, cracks or failure due to support or reinforcing details may be due to ineffective design, metal warpage or growth or fabrication failures. Metal reinforcement of concrete, if made too stiff, may cause rupture in the plane of the reinforcement because of differential expansion. Vibration may initiate or accelerate mechanical failure. Where erosion resistance is necessary the materials and details must be selected accordingly. In fluid catalyst vessels, insulating and refractory concrete linings have shown adequate resistance.

Avoidance of structural deterioration requires the selection of materials and cements which remain stable under the maximum temperature and do not suffer undue loss of strength or undergo significant change in volume. Some insulations containing asbestos become friable and are gradually reduced to powder with prolonged heating at 850°F and higher. In addition all unfired castables containing portland or alumina cement as the binder are structurally weak between 1200 and 1800 F.

Chemical deterioration includes corrosion, oxidation, chemical reaction or other chemistry change as a result of exposure to service conditions. Corrosion is possible in certain atmospheres such as flue gas where even minute amounts of sulphur, oxidized to acid may attack non-resistant materials or aggregates. This may occur during off-stream periods.

The effect of carbon deposition on conductivity has been discussed in Section II. In the case of brick or concrete containing iron oxides operating in an atmosphere containing carbon monoxide, the literature shows that carbon deposition may be accompanied by disruption of the concrete or brick. In this case a chemical decomposition of the carbon monoxide occurs in the presence of iron oxides as a catalyst and the resulting carbon is deposited in such a way that it exerts a mechanical disruptive force. The favorable temperature range for this reaction is between 800 and 1800 F. Curiously however, no deterioration of this kind has been observed to the authors knowledge in fluid catalytic cracker regenerator service, and iron-free aggregates and cements are not at present considered necessary for that service. Carbon deposition which is not the result of such a chemical reaction does not seem to affect the structural integrity of the refractory and may enhance it.

Operating variables include overheating, abrupt pressure or temperature changes and cyclic operation. Overheating has been a cause of insulation deterioration and eventual failure where the material was selected ignoring occasional temperatures above the design level. Experience shows that if a process is exothermic or if there is any possibility of excess temperature due to operational mistakes, emergency or start-up or shut-down operations the materials should be selected with a proportionate safety margin. Manufacturers service temperature ratings are usually based on so-called hot face temperatures and not for the limiting temperature through the entire thickness; in addition the ratings are usually optimistic and correspond to the most favorable conditions. The effect of overheating varies; with some materials limited periods can be sustained without significant damage; others undergo a gradual breakdown while still others may suffer sudden complete disintegration. A given insulation may respond differently in an oxidizing than in a reducing atmosphere.

Failure due to overstress, short time or gradual creep is usually the result of improper support design or overheating.

IV. PERFORMANCE IN SERVICE

In this section the authors will discuss factors other than those covered in Sections II and III which markedly affect performance. These are:

1. Vapor flow through or behind insulation
2. Local turbulence or pressure drops
3. Support arrangement
4. Effect of external insulation

Vapor flow through or behind the insulation will seriously destroy its effectiveness. Accordingly the design and materials chosen must effectively guard against it. The possibility of such flow increases with the pressure drop per foot of the flowing medium and with porosity or lack of resistance to flow within the insulatior

Three situations can be considered:

1. Vessels or piping subject to internal flow without internals.
2. Vessels with fluid catalyst beds.
3. Vessels with fixed catalyst beds.

In the authors' experience vessels with no internals operating at low velocities have given no particular trouble of this nature. Piping operating at considerably higher velocities and with higher proportionate area of insulation to total cross-section, has given trouble particularly when low density insulations are used. In some cases insulation has been swept out.

Vessels containing fluid catalyst beds have occasionally shown evidence of flow through or behind the insulation due probably to the combination of unit pressure drop and static differential head.

Vessels containing fixed catalyst beds usually involve higher unit pressure drop, which is a function of velocity and catalyst particle size and shape, and vapor flow through or behind the insulation must be carefully guarded against. When trouble of this kind has been encountered it has been overcome by incorporation of better details to assure good contact of the insulation with the shell, or by the use of denser materials or both in some cases; other cases have required the installation of a tight metal shield. Measures to prevent or control vapor flow through or behind insulation are discussed in Section V. Experience to date has not been entirely consistent and is difficult to interpret satisfactorily, but it is the authors' opinion that when the insulating material is concrete or brick with a density of 60 lbs per cubic foot or more, vapor flow between the insulation and the shell rather than flow through the pores of the insulation itself is the factor which must be guarded against to prevent overheating. The lesser problem with fluid as compared with fixed catalyst beds is probably due to the lower superficial velocity and the fact that the greatest part of the unit pressure drop goes to support the weight of the suspended particles; the tendency to deposit material at locations of directional change, horizontal runs or de-aerated areas with consequent plugging also helps.

Local overheating due to vapor flow behind the insulation has occurred at areas of high local pressure drop and turbulence, in all applications, when the details did not provide adequate local shielding. Typical locations are tee connections in pipe lines, nozzle entrances in pressure vessels and around the edge of grids in fluid catalyst vessels. A typical instance of vapor flow behind an insulating concrete lining occurred recently in a fluid catalytic cracking regenerator directly above the grid resulting in roving hot spots. The insulation on successive inspections appeared in excellent condition; however it was possible to demonstrate by means of an air hose that air flow behind the insulation was possible. It is logical to suppose that similar gaps existed elsewhere on the vessel lining yet the localized pressure drop across the grid seemed to be the initiating influence of the flow causing hot spots.

The manner in which the insulation is supported greatly influences the possibility of vapor flow behind the insulation. Details which provide sectional support and which maintain the insulation in close contact with the shell generally provide the best performance. This is discussed further in Section V.

Vessels which have both internal and external insulation would be expected to be more sensitive to overheating than vessels which have only internal insulation, and experience seems to bear this out. The blanket, block or plastic external insulations normally used are fairly efficient even in minimum practical thicknesses. Insulation for internal use on the other hand must be fairly rugged and is generally less efficient thermally. With such combinations the shell metal temperature runs much higher than with the bare shell and a given percentage increase in the internal conductivity generally results in a greater metal temperature rise. In addition with a bare shell there is generally a greater temperature margin available for overheating before the shell strength is seriously reduced and such areas can also be readily detected and provided with remedial measures. When using external insulation therefore even greater attention should be given to the design.

V. DESIGN CONSIDERATIONS

A. Selection of Internal Insulation Materials

The insulation material must be selected with due consideration to the factors previously discussed considering mis-operation and short time emergency conditions as well as nominal design conditions. The major factors are conductivity, including the effect of gas and pressure, corrosion, erosion, porosity, coking, spalling and cracking tendencies, as well as possible deterioration, including CO-attack. When used in contact with catalyst its effect on the insulation and vice-versa should be checked. The answer in some cases may be a combination of materials, a low conductivity material against the shell and a stronger and more rugged material on the inside. From the remarks previously made it is clear that the conductivity of the nominally more efficient but more porous insulations is likely to be more seriously affected by coke, hydrogen, pressure or vapor permeation. These materials are usually subject to greater deterioration due to overheating. A careful and comprehensive evaluation should therefore be made.

Insulating and refractory concrete linings suitably installed have given good service in the temperature range of 900 to 1150°F. in petroleum vessel applications with short time operational upset temperatures of 1400 F and higher. In fluid catalyst vessel service the denser grades of insulating concrete appear to possess satisfactory erosion resistance except in localized high velocity zones.

B. Metal Inclusions

Metal inclusions due to their high conductivity can appreciably increase the overall conductivity of an insulation assembly. Support

studs, vapor barrier ring etc. usually extend through part of the insulation thickness or to the inside and over this depth affect heat flow in proportion to their area and conductivity. Usually these parts are intimately welded to the shell and the following relation for the combined conductivity, while not precise, gives satisfactory results for design purposes:

$$k = k_1 \frac{(A_1)}{(A_1 + A_m)} + K_m \frac{(A_m)}{(A_1 + A_m)}$$

where k = conductivity and A = area; the subscripts 1 and m denote insulation and metal respectively.

Metal attachments of substantial cross-section going through the insulation exert local effects and require special attention as noted in section K below.

C. External - vs - No External Insulation

This item was discussed briefly in Section IV in which the economic and safety advantage of omitting external insulation was pointed out. It is re-emphasized that external insulation should be avoided whenever possible in the interest of safety. External insulation is sometimes necessary to prevent a shell temperature which would result in an unacceptable corrosive condensate condition on the inside; however, toleration of slight corrosion is preferable when the condition is mild and consideration should be given to protective linings in more severe cases. External insulation should not be used merely for protection of operators from hot surfaces; expanded metal shields can be provided as necessary and retain the the advantage of full view of the external surface.

D. Corrosion of Shell due to Condensate

As mentioned above, if the shell metal temperature falls below the dewpoint of the internal vapor, condensate will form which may or may not be corrosive depending on the service. No trouble of this kind has been encountered to date in fluid catalytic cracking regenerator or reactor service despite the almost universal absence of external insulation. This may be due to the low desulphurization properties of the catalyst, minimizing oxidation of sulphur fractions. In a few cases a 1" thick layer of dense gunnite concrete with wire mesh reinforcing has beer applied to the inside of the shell as additional protection against condensate corrosion. In fixed bed hydrofomer service condensate corrosion has been encountered in flue gas lines at low temperature stagnant flow areas, and the reactors, in which both reaction and regeneration takes place, have been externally insulated to guard against such corrosion. However, the rate of corrosion is undoubtedly connected with the sulphur content of the feed and the desulphurization properties of the catalyst; on some of the current reformer and fluid hydroformer vessels, external insulation is omitted.

E. Support Details

As mentioned in Section IV sectionally supported construction has given the best performance. Typical insulating concrete installations are shown in Figures 1 and 2, Figure 2 involving the use of a hexagon pattern steel surface-retaining grating. Sectional support is provided by flash welded studs which are on close centers, usually 9 to 12". Vapor barrier rings, when used, provide additional support. No expansion joints are necessary in the insulating concrete but the inner hex steel reinforced refractory layer of Figure 2 is generally panalled with expansion gaps between panels. (See following Section F).

Other sectionally supported construction which has been successfully used involves the use of block insulation supported on rings at regular intervals, wired to the shell and covered with a supported tile facing; however, the softer insulation is more easily eroded or possibly damaged by vibration where such effects are present.

Linings consisting of an insulating or refractory brick column supported from the bottom head are prone to permit vapor by-passing, depending on the unit pressure drop, since a gap may open up at the top of the column and also between the outside diameter of the brick column and the inside diameter of the shell. Such brick columns, however, have given very satisfactory performance as the inner facing for a sectionally supported block or insulating concrete lining, particularly for temperatures over 2000°F.

In addition to providing insulation support, the design should also maintain the insulation in intimate contact with the shell, as insulating concrete or plastic insulations will not maintain a satisfactory bond with steel. The excellent performance of the detail of Figure 2 is due in part to accomplishing this objective; the Figure 1 detail is not as effective.

F. Metal Grid at Inner Surface

The use of a 3/4" deep x 14 gage hexagonal steel grating within the surface layer of refractory or insulating concrete has been very effective in providing low maintenance linings in fluid catalytic cracking regenerator and reactor service at temperatures up to 1150°F. Expanded metal has also been tried but without equal results. As used by the authors' company the hex steel is applied in panels 2' x 3' or 3' x 3'-4" usually with a 1/8" expansion gap between panel edges. In some cases the panel edges have been banded by welding on flat bars but the performance of unbanded panels has also been good so that the cost of banding is not justified. The first installation of this type has given maintenance free service in a regenerator for eight years; however the steel grating now shows serious oxidation loss and may require replacement in the near future. When used in panels the grating shows a tendency to curl at the edges in service. This curling occurs at the ends of the long bars (strong direction of grating) but causes no difficulty provided the panel is adequately

attached to the studs located near the ends. Some installations have been made with larger panel sizes and with reduction or elimination of expansion gaps and other installations have had the ends of each steel panel welded or otherwise fastened to each other to provide a monolithic inner facing. The authors do not have information relative to performance of this type installation which should be judged only after several years and cycles of service.

The major practical benefit of the steel grating surface seems to be that it locks the surface refractory concrete in position and prevents surface cracking and spalling. It is also less subject to extensive failure due to faulty installation. Even so when placing the refractory concrete a gap of approximately 1/4" should be provided behind the grating so that the refractory will flow behind and obtain an added key effect.

G. Vapor Shields and Barriers

When pressure drop relations become severe an effective metal vapor shield will provide positive protection against vapor flow through or behind the insulation so long as it can be maintained tight in service. Experience indicates that when the pressure drop per foot exceeds about 0.25 psi in fixed bed catalyst service consideration should be given to such shielding. The authors do not wish to imply that satisfactory design cannot be developed for higher pressure drops without shields, as concrete linings without shields have performed satisfactorily at pressure drops up to about 1 psi per foot; however experience to date is mixed and inadequate. Therefore when a shield can be satisfactorily provided it seems the best choice.

To be fully effective a metal shield must be sealed to the shell at one end and run in front of the insulation for the full length of the high pressure drop zone or to the start of the next shield. The other end of the shield is left open to provide for differential expansion and equalize vapor pressures across the sheild. A typical installation used for 1400 and 1800°F. superheated steam piping service shown in Figure 3 This construction may also be used in vessels or a single cylindrical shield may be used as shown in Figure 4. The design of the shields must be carefully worked out considering differential expansion, sudden depressuring which may cause collapse, venting and drainage.

In lieu of vapor shields as described above, barrier rings seal welded to the shell are sometimes used at regular intervals, usually about 2 feet, to inhibit vapor flow. Such rings are not very effective against flow through the insulation and will be only partially effective in reducing flow behind the insulation should the details permit a gap to form. They should not be considered an effective substitute for a vapor shield.

H. Local Shields

Local vapor tight shields should be provided at nozzle entrance and exit points. Metal shields are also useful at points of local thermal shock e.g. near internal water sprays where there is danger of water impingement.

J. Nozzle Construction

Nozzle connections often involve a transition from internally insulated to uninsulated construction. The details must provide the desired temperature reduction. Figure 5 shows a typical welding type transition. In Case 2 of the Appendix, a formula is derived for establishing a nozzle length which will provide the desired temperature transition and avoid local overheating of the pressure shell.

K. Through Metal for Internals

Vessel details often require heavy metal connections through the insulation for internal parts. A typical example is the cyclone plenum chamber in catalytic cracking regenerators. To avoid local overheating of the shell these metal parts must be suitably insulated. In Case 1 of the Appendix a formula is derived for calculating the local temperature of the shell at such details.

L. Design Margin against Overheating

No guiding rule can be suggested for this item. It is nevertheless an important subject. The design metal temperature selected should at least provide sufficient allowance to take care of the probable increases in conductivity due to gas, pressure and included metal plus a suitable margin for deterioration, coking, etc. A minimum assumption which the authors have used is to assume the internal conductivity of insulating concrete to be at least 50% higher than the manufacturers rating when used in flue gas or equivalent service and at least 100% higher when used in hydrocarbon service involving high hydrogen or coking conditions. The factor used should be in step with the porosity and ruggedness of the insulation and the severity of the service. Individual factors for coking and hydrogen and pressure are not warranted as they should not be directly additive as mentioned in Section II. For equivalent safety a higher design temperature margin would be needed when external insulation is used than when it is omitted; in addition the externally insulated vessel should be provided with much more elaborate metal temperature instrumentation. The question as to whether there should be some minimum metal design temperature as a percentage of the internal temperature or what alternate consideration there should be against the possibility of a partial loss of a sizable segment of the lining is an open one; at present designs are treated individually.

VI. ACKNOWLEDGEMENT

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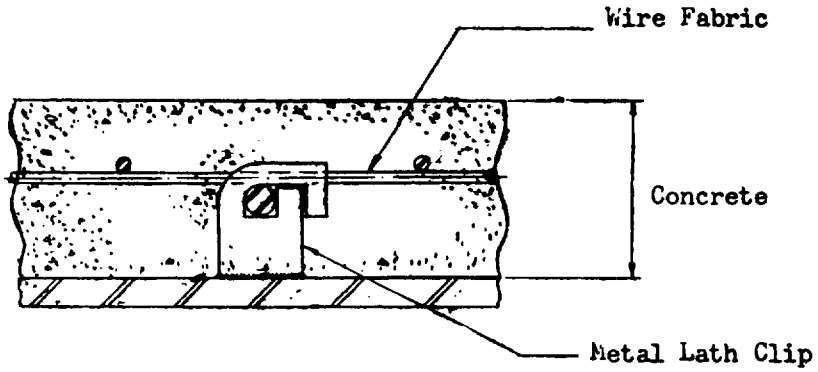

FIGURE 1

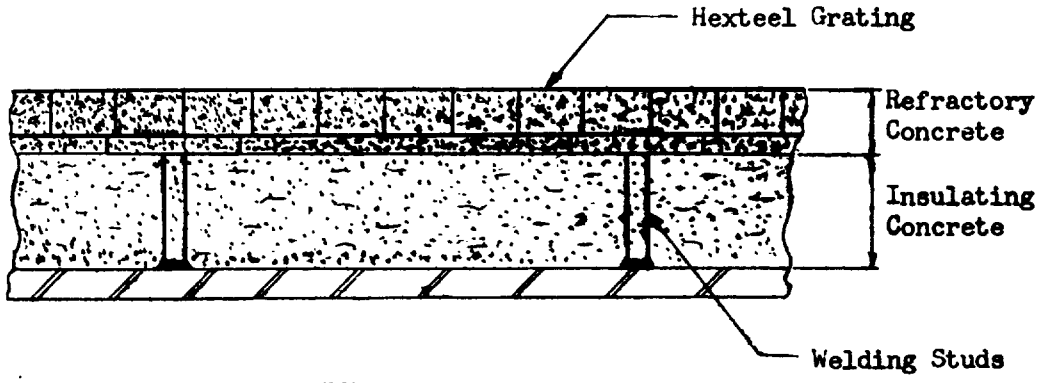

FIGURE 2