NOTATION

C_1 = constant defined in Equation (7)
C_2 = constant defined in Equation (8)
G = mass velocity, lb./(hr.)(sq.ft.)
k = thermal conductivity, B.t.u./(hr.)(ft.)(°F.)
p = pressure, lb.$_f$/sq.ft.abs.
q = heat flux, B.t.u./(hr.)(sq.ft.)
r = radius, ft.
R = ideal gas constant, (ft.)(lb.$_f$)/(lb.)(°R.)
S = group of variables defined in Equation (14)
T = temperature, °R. or °F.
ΔT = temperature difference, °F.
y = distance from the wall, ft.

Greek Letters

θ = bubble contact angle
λ = heat of vaporization, (ft.)(lb.$_f$)/lb.
ρ = density, lb./cu.ft.
σ = surface tension, lb.$_f$/ft.
ξ = group of variables defined in Equation (13)

Subscripts and Superscripts

b = bubble nucleus
c = cavity
$'$ = coordinates of points of intersection of the superheat curve and temperature profile
L = liquid phase
s = property evaluated at the saturation condition
v = vapor phase
w = property or condition at the wall

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Vapor-Liquid Equilibria for Five Cryogenic Mixtures

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Phase equilibrium data have been obtained for the binary systems nitrogen-argon and nitrogen-carbon monoxide at 83.82°K. and for the systems nitrogen-methane, argon-methane, and carbon monoxide-methane at 90.67°K. Total pressures and compositions of both phases were measured. Parameters have been calculated for the Redlich-Kister and Wilson equations for the excess Gibbs energies of the mixtures. The data are thermodynamically consistent within experimental error.

Information on the vapor-liquid equilibria of cryogenic mixtures is important both for design purposes and as a test of theories of solutions. The relatively simple molecules involved most nearly conform to the requirements of current theoretical work; however, the experimental measurements are made more difficult by the necessity of operating at low temperatures.

Equilibrium data on the systems nitrogen-argon and nitrogen-carbon monoxide have been obtained at 83.82°K. The mixtures nitrogen-methane, argon-methane, and carbon monoxide-methane have been studied at 90.67°K. In all cases, measurements were made of the total pressure and the compositions of liquid and vapor phases (P, x, y). In this way, the thermodynamic consistency of the data can be tested.

Some data for these systems are already available in the literature, although in most investigations only total pressure and liquid phase composition (P-x) data have been taken, and in this case no thermodynamic consistency test can be performed. In some previously publisher

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work, the temperature of measurement differed from that of the present investigation.

The data reported here have been tested thermodynamically and appear consistent within the very small estimated experimental errors.

EXPERIMENTAL APPARATUS

The basic apparatus used in this work has been described by Eckert and Prausnitz (*4*). The vapor in the equilibrium cell was circulated through an external pump to enhance the attainment of equilibrium and to provide for sampling of the vapor phase. Liquid sampling was accomplished through the use of extended needle valves which could extract quite small volumes relative to the cell capacity.

Temperature control has been added to the previously described apparatus (*12*); variations of less than 0.05°K. could be maintained for long periods of time. Thermocouples were provided in the liquid and vapor regions of the equilibrium cell, and temperature differences between these thermocouples were always less than 0.03°K. A bed of copper shavings above the vapor inlet at the bottom of the cell provided for good mixing of the returning vapor stream with the liquid.

Analysis of liquid and vapor compositions was performed by the use of vapor chromatography. A Beckman GC2-A chromatograph and a 6-ft. Linde 5A molecular sieve column were used for all analyses. Determinations on prepared blends showed the analytical procedure capable of measuring compositions to within about 0.3% over most of the composition range. Pressure measurements up to about 850 mm. Hg were performed with a mercury manometer and a Wild Heerbrugg KM-274 cathetometer; higher pressures were measured on either a 0 to 30 lb./sq.in.abs. or a 0 to 300 lb./sq.in. gauge Heise gauge.

MATERIALS

The supplier and purity of each gas used were:

Nitrogen	Matheson	99.996%
Argon	Linde	99.995%
Carbon monoxide	Linde	99.8%
Methane	Matheson	99.98%

Carbon monoxide was purified further before it was condensed into the cell by freezing out the main impurity, carbon dioxide.

RESULTS

Tables 1 to 5 present the equilibrium data for the five binary systems. Here P represents total pressure. The temperature of each individual run was within 0.03°K. of the temperature indicated. Liquid and vapor compositions are believed accurate to approximately two parts in the last place reported. Pressures in the range 0 to 850 mm. Hg were measured to about ± 0.02 mm. Hg; in the range 850 to 1,550 mm. Hg to ± 0.4 mm. Hg; and above 1,550 mm. Hg to ± 4 mm. Hg.

The molar excess Gibbs energies g^E at each liquid composition have been calculated and are reported along with the data in Tables 1 to 5. The excess Gibbs energy is related to the activity coefficients by

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{1}$$

The activity coefficients have been calculated from well-known equations (see, for example, reference *13*) valid at low pressures:

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 P_1^{\text{sat}}} + \frac{(B_{11} - v_1)(P - P_1^{\text{sat}})}{RT} + \frac{P\delta y_2^2}{RT} \tag{2}$$

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 P_2^{\text{sat}}} + \frac{(B_{22} - v_2)(P - P_2^{\text{sat}})}{RT} + \frac{P\delta y_1^2}{RT} \tag{3}$$

TABLE 1. PHASE EQUILIBRIA FOR THE NITROGEN(1)-ARGON(2) SYSTEM AT 83.82°K.

Mole % nitrogen			
Liquid	Vapor	P, mm. Hg	g^E, cal.-mole^{-1}
0	0	517.02	0
5.80	17.0	590.88	2.14
8.48	23.9	623.90	2.27
14.8	36.0	698.05	4.25
19.2	43.5	747.72	4.39
27.9	54.0	841.58	7.01
30.0	56.2	864.2	7.60
43.4	68.8	998.6	7.92
49.6	73.5	1060.2	8.08
55.8	77.5	1117.0	7.92
62.9	82.0	1183.8	7.10
65.1	83.0	1203.9	7.40
68.2	85.1	1233.4	6.32
75.7	88.6	1303.2	6.23
79.6	90.5	1338.4	5.53
80.9	91.3	1350.8	4.96
87.6	94.7	1411.8	2.85
91.2	96.0	1445.4	2.73
100.0	100.0	1528.2	0

Fitted parameters		Std. dev. in g^E, cal.-mole^{-1}
Redlich-Kister equation		
One-term	$A_1 =$ 32.28 cal.-mole^{-1}	0.41
Two-term	$A_1 =$ 32.38 cal.-mole^{-1}	0.39
	$A_2 =$ —1.56 cal.-mole^{-1}	
Three-term	$A_1 =$ 32.40 cal.-mole^{-1}	0.39
	$A_2 =$ —1.57 cal.-mole^{-1}	
	$A_3 =$ —0.15 cal.-mole^{-1}	
Wilson equation		
	$\Lambda_{12} =$ 0.8184	0.39
	$\Lambda_{21} =$ 0.9961	
	$\lambda_{12} - \lambda_{11} =$ —7.80 cal.-mole^{-1}	
	$\lambda_{12} - \lambda_{22} =$ 41.83 cal.-mole^{-1}	

TABLE 2. PHASE EQUILIBRIA FOR THE NITROGEN(1)-CARBON MONOXIDE(2) SYSTEM AT 83.82°K.

Mole % nitrogen			
Liquid	Vapor	P, mm. Hg	g^E, cal.-mole^{-1}
0	0	957.8	0
9.91	16.0	1032.2	1.91
19.2	28.3	1097.4	3.62
26.8	37.8	1147.6	4.23
44.5	56.0	1254.1	5.22
59.1	68.5	1333.2	5.26
71.8	78.7	1397.9	4.43
85.8	89.5	1465.1	2.65
93.2	95.0	1498.7	1.39
100.0	100.0	1528.2	0

Fitted parameters		Std. dev. in g^E, cal.-mole^{-1}
Redlich-Kister equation		
One-term	$A_1 =$ 21.73 cal.-mole^{-1}	0.10
Two-term	$A_1 =$ 21.73 cal.-mole^{-1}	0.10
	$A_2 =$ —0.26 cal.-mole^{-1}	
Three-term	$A_1 =$ 21.47 cal.-mole^{-1}	0.09
	$A_2 =$ —0.22 cal.-mole^{-1}	
	$A_3 =$ 1.45 cal.-mole^{-1}	
Wilson equation		
	$\Lambda_{12} =$ 0.9131	0.10
	$\Lambda_{21} =$ 0.9589	
	$\lambda_{12} - \lambda_{11} =$ 13.89 cal.-mole^{-1}	
	$\lambda_{12} - \lambda_{22} =$ 8.24 cal.-mole^{-1}	

TABLE 3. PHASE EQUILIBRIA FOR THE NITROGEN(1)-METHANE(2) SYSTEM AT 90.67°K.

Mole % nitrogen Liquid	Mole % nitrogen Vapor	P, mm. Hg	g^E, cal.-mole^{-1}
0	0	87.78	0
13.3	88.9	718.8	14.0
20.0	92.0	949.0	19.4
23.8	92.8	1062.7	26.9
34.1	94.7	1337.3	32.2
42.9	95.9	1545.2	30.9
53.1	96.8	1769	31.3
62.8	97.5	1981	30.0
81.1	98.5	2384	24.3
95.2	99.5	2736	8.7
100.0	100.0	2870	0

Fitted parameters		Std. dev. in g^E, cal.-mole^{-1}
Redlich-Kister equation		
One-term	$A_1 = 133.5$ cal.-mole^{-1}	2.3
Two-term	$A_1 = 134.3$ cal.-mole^{-1}	2.2
	$A_2 = 7.64$ cal.-mole^{-1}	
Three-term	$A_1 = 129.2$ cal.-mole^{-1}	1.9
	$A_2 = 11.71$ cal.-mole^{-1}	
	$A_3 = 38.53$ cal.-mole^{-1}	
Wilson equation		
	$\Lambda_{12} = 0.7205$	2.2
	$\Lambda_{21} = 0.6035$	
	$\lambda_{12} - \lambda_{11} = 48.38$ cal.-mole^{-1}	
	$\lambda_{12} - \lambda_{22} = 101.68$ cal.-mole^{-1}	

TABLE 4. PHASE EQUILIBRIA FOR THE ARGON(1)-METHANE(2) SYSTEM AT 90.67°K.

Mole % argon Liquid	Mole % argon Vapor	P, mm. Hg	g^E, cal.-mole^{-1}
0	0	87.78	0
8.32	59.5	200.33	4.69
11.7	67.7	242.89	6.33
20.4	79.2	345.48	10.35
28.9	84.8	437.23	15.12
41.1	89.8	557.02	16.90
50.8	92.4	644.80	16.95
71.2	96.1	819.11	14.12
85.2	98.0	939.1	9.62
91.3	98.8	993.4	6.36
100.0	100.0	1075.7	0

Fitted parameters		Std. dev. in g^E, cal.-mole^{-1}
Redlich-Kister equation		
One-term	$A_1 = 69.30$ cal.-mole^{-1}	0.69
Two-term	$A_1 = 69.70$ cal.-mole^{-1}	0.59
	$A_2 = 4.95$ cal.-mole^{-1}	
Three-term	$A_1 = 69.68$ cal.-mole^{-1}	0.59
	$A_2 = 4.97$ cal.-mole^{-1}	
	$A_3 = 0.16$ cal.-mole^{-1}	
Wilson equation		
	$\Lambda_{12} = 0.9423$	0.59
	$\Lambda_{21} = 0.6977$	
	$\lambda_{12} - \lambda_{11} = 46.73$ cal.-mole^{-1}	
	$\lambda_{12} - \lambda_{22} = 28.83$ cal.-mole^{-1}	

TABLE 5. PHASE EQUILIBRIA FOR THE CARBON DIOXIDE (1)-METHANE(2) SYSTEM AT 90.67°K.

Mole % carbon dioxide Liquid	Mole % carbon dioxide Vapor	P, mm. Hg	g^E, cal.-mole^{-1}
0	0	87.78	0
4.22	60.8	213.70	1.8
11.3	80.0	404.22	11.6
17.8	85.9	558.28	20.4
25.3	89.8	715.46	23.3
44.4	94.3	1046.2	28.1
51.7	95.3	1154.8	28.0
67.1	97.0	1375.6	23.8
80.1	98.0	1567	20.6
89.2	99.1	1707	8.5
100.0	100.0	1893	0

Fitted parameters		Std. dev. in g^E, cal.-mole^{-1}
Redlich-Kister equation		
One-term	$A_1 = 115.9$ cal.-mole^{-1}	2.1
Two-term	$A_1 = 115.6$ cal.-mole^{-1}	1.9
	$A_2 = -10.51$ cal.-mole^{-1}	
Three-term	$A_1 = 114.5$ cal.-mole^{-1}	1.9
	$A_2 = -10.10$ cal.-mole^{-1}	
	$A_3 = 6.53$ cal.-mole^{-1}	
Wilson equation		
	$\Lambda_{12} = 0.5706$	1.9
	$\Lambda_{21} = 0.8496$	
	$\lambda_{12} - \lambda_{11} = 92.36$ cal.-mole^{-1}	
	$\lambda_{12} - \lambda_{22} = 38.10$ cal.-mole^{-1}	

TABLE 6. SECOND VIRIAL COEFFICIENTS USED IN DATA REDUCTION

System	T, °K.	B_{11}, cc.-mole^{-1}	B_{22}, cc.-mole^{-1}	B_{12}, cc.-mole^{-1}
Nitrogen(1)-argon(2)	83.82	−229.8	−248.1	−243.0
Nitrogen(1)-carbon monoxide(2)	83.82	−229.8	−262.3	−250.2
Nitrogen(1)-methane(2)	90.67	−198.0	−456.9	−303.5
Argon(1)-methane(2)	90.67	−216.3	−456.9	−312.2
Carbon monoxide(1)-methane(2)	90.67	−225.3	−456.9	−326.9

TABLE 7. TEST FOR THERMODYNAMIC CONSISTENCY OF DATA

System	T, °K.	Deviation in P, mm. Hg Maximum	Deviation in P, mm. Hg Standard	Deviation in y Maximum	Deviation in y Standard
Nitrogen-argon	83.82	1.3	0.5	0.005	0.002
Nitrogen-carbon monoxide	83.82	0.4	0.3	0.003	0.002
Nitrogen-methane	90.67	3	1.3	0.003	0.001
Argon-methane	90.67	0.3	0.1	0.002	0.001
Carbon monoxide-methane	90.67	2	1.0	0.003	0.002

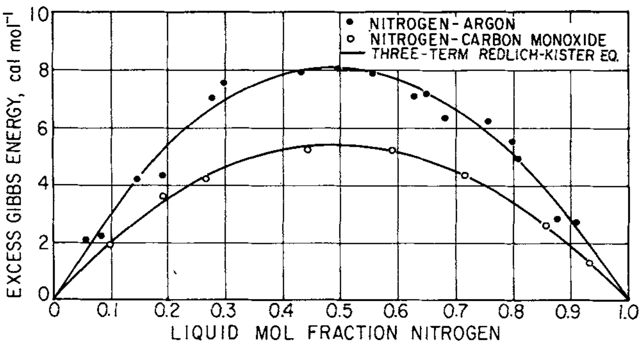

Fig. 1. Excess Gibbs energy of nitrogen mixtures at 83.82°K.

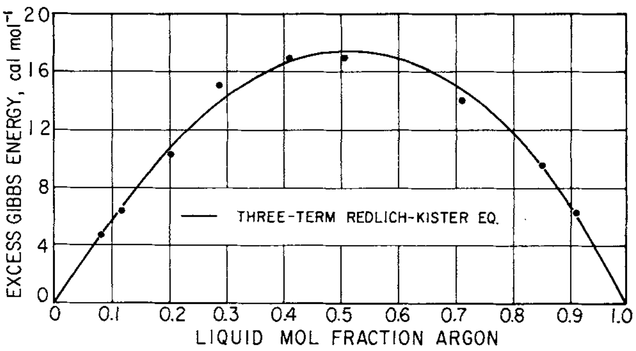

Fig. 2. Excess Gibbs energy of argon-methane system at 90.67°K.

P_i^{sat} represents the saturation pressure of pure component i, B_{ii} the second virial coefficient of pure i, B_{ij} the mixed second virial coefficient for the i-j pair, v_i the liquid molar volume of i, and $\delta \equiv 2B_{12} - B_{11} - B_{22}$. x and y are the liquid and vapor mole fractions, respectively. Liquid molar volumes were taken from the literature (*3, 7, 9*). Pure component virial coefficients were calculated by Pitzer's method (*5*) and are summarized in Table 6. The mixed virial coefficients were calculated by a method reported previously (*10*).

EQUATIONS FOR THE EXCESS GIBBS ENERGY

The excess Gibbs energies calculated from the P-x-y data have been fitted to the Redlich-Kister and Wilson equations. The Redlich-Kister equation (*11*) is:

$$g^E = x_1x_2(A_1 + A_2\,[x_1 - x_2] + A_3\,[x_1 - x_2]^2 + \ldots.) \tag{4}$$

The equation truncated after the A_1 coefficient is referred to as the one-term equation, etc. The Wilson equation (*8, 14*) is:

$$\frac{g^E}{RT} = -\,x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \tag{5}$$

As shown by Wilson (*14*), the parameters Λ_{12} and Λ_{21} are related to characteristic energies which may be reasonably temperature independent over a small temperature range:

$$(\lambda_{12} - \lambda_{11}) = -\,RT \ln\left(\frac{v_1}{v_2}\Lambda_{12}\right) \tag{6}$$

$$(\lambda_{12} - \lambda_{22}) = -\,RT \ln\left(\frac{v_2}{v_1}\Lambda_{21}\right) \tag{7}$$

The fitted coefficients for the one-, two-, and three-term Redlich-Kister equations and for the Wilson equation are presented along with the data in Tables 1 to 5. Standard deviations of the fitted curves from the experimental values are also given. In each case the Wilson equation does as well or better than the two-term Redlich-Kister equation, and only for the nitrogen-methane system is the use of the three-term Redlich-Kister equation a significant improvement. Average errors in g^E arising from experimental uncertainties are estimated to be (in cal.-mole^{-1}) for the various systems: nitrogen-argon, 0.55; nitrogen-carbon monoxide, 0.45; nitrogen-methane, 2.5; argon-methane, 0.9; and carbon monoxide-methane, 2.3. In all cases, errors in g^E are within these limits. Figures 1 and 2 show the experimental values of g^E and the curves based on the three-term Redlich-Kister equation for the nitrogen-argon, nitrogen-carbon monoxide, and argon-methane systems.

COMPARISON WITH PREVIOUS RESULTS

The nitrogen-argon system has been studied by Pool et al. (*9*) at 83.82°K. Their equimolar excess Gibbs energy calculated from P-x data is 8.21 cal.-mole^{-1}; this compares well with our value of 8.1 cal.-mole^{-1}.

The nitrogen-carbon monoxide system has also been studied by Pool et al. (*9*) at 83.82°K. By using P-x data their equimolar g^E is 5.49 cal.-mole^{-1}, differing only slightly from our value of 5.4 cal.-mole^{-1}.

The nitrogen-methane system has been studied by Cines et al. (*2*) at temperatures above 100°K. P-x-y data were taken. By extrapolating their data to 90.67°K., their equimolar g^E is about 3 cal.-mole^{-1} higher than our value.

Argon-methane equilibria have been reported at 86.74°K. by Mathot (*6*). Extrapolation to 90.67°K. leads to an equimolar g^E about 0.5 cal.-mole^{-1} higher than ours.

Data on the carbon monoxide-methane system at 90.67°K. have been reported by Mathot et al. (*7*). The equimolar value of g^E calculated from their P-x data is 28.0 cal.-mole^{-1}. Our value is 28.6 cal.-mole^{-1}.

THERMODYNAMIC CONSISTENCY

Experimental P-x-y data are best tested for thermodynamic consistency by a technique which allows point-by-point comparison with the Gibbs-Duhem equation and which also indicates deviations from consistency in terms of experimental rather than derived quantities. Using Barker's method (*1*), one may use the experimental P-x data to generate a set of P-x-y values consistent with the Gibbs-Duhem equation. Thus, if the P and y values generated by the use of the Gibbs-Duhem equation are compared with those measured experimentally at a particular liquid composition, both requirements are satisfied. In Table 7 the maximum and standard deviations in P and y are given for all five systems. The standard deviations in both P and y are within the experimental errors estimated for each quantity; the data are therefore thermodynamically consistent. In these calculations a three-term Redlich-Kister equation was used to generate the P and y values from Barker's method. The inclusion of higher terms or the use of the Wilson equation does not significantly alter the results.

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NOTATION

A_1, A_2, A_3 = constants for Redlich-Kister equation
B = second virial coefficient

g = molar Gibbs energy
P = pressure
R = gas constant
T = absolute temperature
v = liquid molar volume
x = liquid mole fraction
y = vapor mole fraction

Greek Letters

γ = activity coefficient
δ defined as $2B_{12} - B_{11} - B_{22}$
Λ_{12}, Λ_{21} = Wilson parameters
λ = Wilson energy parameter

Subscripts

i = component i
ij = interaction of i and j
1 = component 1
2 = component 2

Superscripts

E = excess
sat = saturated

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A Fundamental Analysis of Slurry Grinding

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An analytical approach to mathematical expression of the mechanisms involved in typical slurry grinders is presented. Experimental equipment performance is correlated with developed formulas. Results are expressed in terms of fundamental machine and slurry parameters useful in predicting performance and scale-up.

Wet grinding methods are frequently preferred over dry grinding where economic and product considerations permit, because wet grinding generally produces finer particle sized products. In fine dry pulverizing or deagglomerating size ranges, surface forces come into action causing agglomeration or cushioning, with less efficient use of energy. This ultimately limits the particle fineness that can be obtained. The much higher viscosity of the liquid system reduces the mobility of the contained solids and markedly increases the effect of shear forces produced by equipment components, thereby increasing size reduction effects. Another factor which may favor wet grinding is the lowering by the liquid phase of the surface tension (surface free energy) of the solids. This reduces the stress required for fracture (*1*).

As the need for fine grinding increases to supply the demand for fine particle products, reactants, and the like, it is important to obtain a more fundamental definition of the mechanisms involved in wet or slurry grinding. Considerable attention has been given to particle or material grindability, with less to the definition of the grinding mechanisms involved in important types of fine wet grinders and homogenizers available commercially. Comparisons of equipment capabilities in relation to product requirements have largely been empirical and qualitative. Correlations of equipment capabilities have mostly been confined to such relationships as throughput capacity in tons per hour ground to a given fineness, or surface area, per horsepower-hour of energy consumed. Little quantitative fundamental information is available on machine capabilities in relation to specific product fineness variations. The choice of equipment, its design, and operation therefore tend to rest on empirical considerations with specific testing needed to determine results of milling changes.

Analytical approaches are available whose early applications give promise of guiding more surely the selection of kind of equipment and of refining its design or operation to meet specific product requirements better. The criterion of merit proposed for assessing mill capabilities is the calculated shear force generated in consequence of the liquid viscosity of the dispersed mixture and the local velocity gradient prevailing in the active grinding zone of the mill. It is this viscous shear force which disintegrates the solid particulate. Forces controlling agglomeration are probably predominately due to molecular attraction and act over very short distances less than 1 micron (*7*). These forces fall off rapidly as separation distances are increased. Solids cleavage force is therefore the important consideration, rather than total work, which is force times distance. Product particle size should therefore correlate accurately with the magnitude of shear force, which should lend itself to calculation.