P-T border curves in the critical region of the mixture.

The accuracy of the tabulated data is estimated as follows: temperature, ±0.5° C.; pressure, ±2.0 p.s.i.; density, ±0.001 gram per cc. for the liquid and ±0.0001 gram per cc. for the vapor. However, in the critical region, the uncertainty in the values reported may be somewhat greater, because of the difficulty in assessing the accuracy of measurements in this region.

COMPARISON OF RESULTS WITH LITERATURE DATA

The propane–*n*-butane system was studied by Nysewander *et al.* (*7*) and the propane–*n*-pentane system by Sage and Lacey (*9*). An apparatus similar to that employed in this study was used. In Table IX (deposited with ASIS) a comparison is made between the values of the temperature and pressure at the critical point, maximum pressure point, and maximum temperature point reported for these systems and those found in this study. The agreement is moderately good for both systems, but noticeably better for the propane–*n*-pentane system. Table X (deposited with ASIS) compares bubble and dew point data for the propane–*n*-butane system. The dew point pressures of mixtures of low propane content agree moderately well with those found in this study; for mixtures of high propane content, the agreement is less satisfactory. The bubble point pressures show fairly large deviations. This is due to the greater sensitivity of the bubble point pressure, compared to the dew point pressure, to small traces of noncondensable gas in the sample.

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Low Temperature Heat Capacities of 15 Inorganic Compounds

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Smoothed low temperature heat capacities and derived thermodynamic functions for KOH, K_2CO_3, K_2SiO_3, $K_2S_2O_8$, KBH_4, LiCl, $LiBO_2$, Li_2SiO_3, MgS, $Mg(CO_2H)_2$, P_4O_{10}, BPO_4, $SnSO_4$, Na_2SiF_6, and $AlCl_3 \cdot 6H_2O$ are presented at even temperatures. Comparisons with literature data indicate the entropies at 298.15° K. are accurate to at least 1%. Such values are useful in thermodynamic calculations, as evidenced by comparison with estimates based on ion contributions.

DURING THE PAST DECADE and a half, the pioneer automatic adiabatic low-temperature calorimeter described by Stull (*13*) was used for the measurement of the heat capacity of a number of inorganic solids. The precision of measurement attained with this calorimeter was somewhat less than could be achieved with manually operated apparatus. Samples used were the best available within the time limitations of an industrial laboratory; in some cases this meant relatively low purity and in others incomplete characterization. Heat capacity measurements are not highly sensitive to impurities, however, and the smoothed heat capacity data led to third-law entropies of good accuracy as shown by some comparisons with data from other laboratories. Therefore, although the measurements may not warrant a detailed account of individual data points, smoothed tables of thermodynamic functions at even temperatures should prove useful in thermodynamic calculations.

MATERIALS

Reagent grade potassium hydroxide was dried under vacuum at 425° C. Analysis by acid titration indicated 97.8% KOH and 2.2% K_2CO_3.

Reagent grade potassium carbonate was dried at 300° C. The manufacturer's analysis indicating 99.9% purity was accepted.

A sample of potassium metasilicate was prepared from

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stoichiometric amounts of the dried K_2CO_3 and 99.9% silica by reaction under vacuum at 1000° C. in a platinum crucible. Gravimetric analysis gave 39.0% SiO_2 (theory 38.94%) but acidimetry indicated 97.3% purity.

Reagent grade potassium persulfate was 99.9% pure by iodometric titration.

Potassium borohydride from Metal Hydrides, Inc., was 98.1% pure by argentimetric analysis (*2*). According to the manufacturer, the impurities included KOH, $K_2B_2O_4$, and methoxy-substituted borohydride groups.

Reagent grade lithium chloride was dried at 200° C. under vacuum for several hours. The sample analyzed 83.34% chloride (theory 83.63%). The manufacturer's analysis indicated less than 0.1% each of sodium and potassium.

Lithium metaborate was prepared by mixing lithium hydroxide and boric acid in stoichiometric proportions and heating to 900° C. for several hours. Hydrochloric acid titration, mannitol-base titration, and flame spectrophotometric sodium analysis were best fitted by assuming 99.6% $LiBO_2$ with impurities Li_2CO_3, Na_2CO_3, and residual H_2O in about equal amounts.

A sample of lithium metasilicate was prepared from reagent grade lithium carbonate and 99.9% silica by fusion under vacuum at 1200° C. Gravimetric analysis showed 66.7% SiO_2 (theory 66.8%). A few tenths per cent potassium was present according to flame spectrophotometry. X-ray powder patterns showed only lines due to Li_2SiO_3.

Magnesium sulfide was prepared by passing hydrogen sulfide over pure magnesium turnings at 900° C. for 8 hours, followed by a dry nitrogen purge for 20 minutes to remove excess sulfur. The sample analyzed 99.7% pure by iodometric titration for sulfide ion and 99.9% by an acidimetric procedure.

Magnesium formate was 99.3% pure by assay for formate ion. No other characterization was known or attempted.

Phosphorus pentoxide analyzed 99.2% pure by acidimetric titration. The x-ray diffraction pattern showed only lines due to the hexagonal form.

A sample of boron phosphate was prepared by heating stoichiometric amounts of boric acid and phosphoric acid to dryness and igniting at 1100° C. for several hours. X-ray patterns showed only crystalline BPO_4. The apparent purity based on the determination of phosphorus by the phosphomolybdate volumetric method was 99.7% and by the pyrophosphate gravimetric method was 99.2%.

Commercial stannous sulfate was analyzed by standard methods as 54.6% Sn (theory 55.3%) and 44.6% sulfate (theory 44.7%). No further attempts at characterization were made.

Fisher certified reagent sodium fluosilicate was analyzed as 99.8% pure by titration of the fluosilicate ion with 0.1*N* sodium hydroxide. X-ray powder patterns agreed with those published by Cox (*3*).

Reagent grade aluminum chloride hexahydrate was analyzed as 11.17% aluminum (theory 11.17%) and 43.98% chlorine (theory 44.06%).

APPARATUS AND PROCEDURE

The calorimeter has been described in detail (*5, 11, 13*). A brief resumé is given here. Samples were contained in a gold-plated copper container of about 65-cc. volume. Re-entrant wells were provided for a platinum resistance thermometer ($R_o = 93$ ohms) and constantan wire heaters. Silicone grease provided good thermal contact. The thermometer was calibrated by comparison with platinum thermometers calibrated at the National Bureau of Standards. Vertical copper fins bonded to the heater wells provided rapid heat distribution to the sample. One atmosphere of helium gas in the container also served as a heat exchange medium.

The container was surrounded by an adiabatic copper shield. Automatic control of the shield was achieved by feeding the output of Chromel-P *vs.* constantan thermels between sample container and shield to one or more servoamplifiers which controlled the shield heating current. Electrical power input to the sample heater was obtained by alternately recording, on a Brown electronic voltage recorder, the potential drops across the sample heater and across calibrated standard resistances. The sample temperature was recorded continuously on a Leeds & Northrup "high precision" resistance recorder. A pendulum-operated clock, periodically checked against a Berkeley Time Interval meter, Model 500C, automatically timed the duration of electrical heat inputs. Refrigeration for the calorimeter was provided by mounting the assembly in the experimental cavity of a Collins helium cryostat.

In practice, samples were cooled to the lowest possible temperature, 10° to 15° K., and the experimental cavity was evacuated. An equilibrium temperature was recorded, an energy input was made which resulted in a temperature rise, and a final equilibrium temperature was recorded. Another energy input was then carried out, so that the entire temperature range to 300° K. was continuously covered. The heat capacity of the empty container was obtained in separate series of experiments at various times. Determinations of the heat capacity of benzoic acid (Calorimetry Conference standard) served as a check on performance and agreed with standard values as follows: ±3.0% below 20° K., ±1.0% from 20 to 30° K., ±0.5% from 30 to 80° K., and ±0.3% from 80 to 310° K.

All results are reported in terms of the defined calorie ≡ 4.1840 absolute joules and the ice point is taken as 273.15° K.

RESULTS

Smoothed heat capacities and the derived thermodynamic functions are presented in Table I. Experimental measurements extended from at least the lowest temperatures given to 298° K. or above. Extrapolation to 0° K. was usually by a simple T^3 law fit of the measurements in the range 15° to 30° K. Maximum deviation of experimental points from the smooth curve was 0.5% from 298° K. down to 100° K., then gradually increased to 1% at 50° K. and 10% at 15° K. The average deviation is about 40% of these maximum values.

Potassium hydroxide values were corrected for the presence of 2.2% carbonate. No corrections were applied to the remaining data because either they were not necessary or they were of doubtful significance, since impurities were not well characterized.

Several thermal anomalies were observed. Potassium hydroxide had a broad λ-type transition with a heat capacity peak at 227.5° K. Potassium borohydride had a much sharper λ-type transition with a heat capacity peak at 77.0° K. Stannous sulfate exhibited an abrupt jump in the heat capacity at 165° K. but no transitional enthalpy was observed. Sodium fluosilicate showed anomalous behavior as a bump in the heat capacity, reaching a maximum at 275° K. The remaining compounds showed the sigmoid curve typical of inorganic solids.

Table I. Smoothed Thermodynamic Functions in Gibbs per Mole

T, °K.	C_p	S	$\frac{H - Ho}{T}$
Potassium Hydroxide			
20	0.387	0.129	0.095
25	0.756	0.253	0.188
30	1.25	0.433	0.323
40	2.40	0.947	0.695
50	3.62	1.61	1.16
60	4.80	2.38	1.67
70	5.84	3.20	2.19
80	6.73	4.04	2.71
100	8.15	5.70	3.66
120	9.25	7.29	4.50
140	10.15	8.78	5.25
160	10.95	10.19	5.91
180	11.78	11.53	6.52
200	12.89	12.82	7.09
210	13.80	13.47	7.39
220	15.45	14.14	7.71
224	16.79	14.43	7.86
227.40	18.85	14.70	8.01
229	16.15	14.82	8.07
230	15.63	14.89	8.10
234	15.25	15.15	8.23
240	15.15	15.54	8.40
260	15.21	16.75	8.92
280	15.34	17.88	9.38
298.15	15.51	18.85	9.74
Potassium Carbonate			
16	0.465	0.161	0.120
20	0.885	0.306	0.228
25	1.69	0.584	0.435
30	2.83	0.987	0.733
40	5.61	2.18	1.60
50	8.30	3.72	2.68
60	10.74	5.45	3.82
70	12.89	7.28	4.97
80	14.67	9.12	6.07
100	17.30	12.69	8.07
120	19.18	16.02	9.77
140	20.65	19.09	11.22
160	21.85	21.93	12.48
180	22.85	24.56	13.58
200	23.70	27.01	14.55
220	24.49	29.31	15.41
240	25.26	31.47	16.20
260	25.97	33.52	16.93
280	26.72	35.47	17.60
298.15	27.35	37.17	18.17
Potassium Metasilicate			
15	0.530	0.180	0.133
20	1.09	0.404	0.300
25	1.88	0.729	0.532
30	2.82	1.15	0.833
40	4.94	2.25	1.60
50	7.08	3.59	2.48
60	9.11	5.06	3.42
70	10.83	6.59	4.35
80	12.43	8.15	5.27
100	15.12	11.22	6.98
120	17.34	14.18	8.53
140	19.24	17.00	9.92
160	20.88	19.68	11.19
180	22.25	22.22	12.35
200	23.47	24.63	13.40
Potassium Metasilicate			
220	24.54	26.92	14.36
240	25.55	29.09	15.25
260	26.52	31.18	16.08
280	27.46	33.18	16.86
298.15	28.30	34.93	17.53
Potassium Persulfate			
15	1.59	0.568	0.421
20	3.18	1.23	0.905
25	5.12	2.14	1.55
30	7.28	3.27	2.32
40	11.59	5.97	4.11
50	15.55	8.99	6.01
60	18.94	12.13	7.89
70	21.80	15.27	9.68
80	24.22	18.34	11.35
100	28.20	24.20	14.34
120	31.45	29.63	16.93
140	34.24	34.70	19.21
160	36.80	39.44	21.25
180	39.27	43.91	23.11
200	41.56	48.17	24.85
220	43.66	52.23	26.46
240	45.73	56.12	27.98
260	47.66	59.86	29.42
280	49.45	63.46	30.79
298.15	50.93	66.61	31.97
Potassium Borohydride			
15	0.175	0.077	0.040
20	0.554	0.177	0.120
25	1.04	0.351	0.252
30	1.60	0.589	0.430
40	2.88	1.22	0.878
50	4.28	2.01	1.42
60	5.82	2.93	2.02
70	7.27	3.94	2.67
80	8.58	5.68	3.99
100	10.42	7.80	5.10
120	12.08	9.85	6.12
140	13.56	11.82	7.08
160	14.96	13.72	7.98
180	16.29	15.56	8.83
200	17.60	17.35	9.64
220	18.94	19.09	10.43
240	20.26	20.79	11.19
260	21.52	22.46	11.94
280	22.66	24.10	12.66
298.15	23.50	25.55	13.30
Lithium Chloride			
15	0.044	0.017	0.012
20	0.131	0.038	0.029
25	0.334	0.087	0.068
30	0.58	0.168	0.131
40	1.31	0.426	0.327
50	2.24	0.815	0.613
60	3.23	1.31	0.966
70	4.18	1.88	1.36
80	5.08	2.50	1.77
100	6.62	3.80	2.59
120	7.77	5.12	3.36
140	8.68	6.39	4.06
160	9.38	7.59	4.68
180	9.90	8.73	5.24
Lithium Chloride			
200	10.32	9.80	5.72
220	10.67	10.80	6.16
240	10.97	11.74	6.55
260	11.21	12.63	6.90
280	11.40	13.46	7.21
298.15	11.58	14.19	7.47
Lithium Borate			
15	0.051	0.013	0.013
20	0.138	0.039	0.032
25	0.261	0.082	0.065
30	0.418	0.143	0.110
40	0.833	0.317	0.237
50	1.35	0.557	0.406
60	1.94	0.855	0.612
70	2.55	1.20	0.845
80	3.19	1.58	1.10
100	4.50	2.43	1.65
120	5.79	3.37	2.23
140	7.02	4.35	2.83
160	8.19	5.37	3.43
180	9.28	6.40	4.02
200	10.31	7.43	4.60
220	11.27	8.46	5.16
240	12.17	9.48	5.71
260	13.00	10.48	6.24
280	13.77	11.48	6.75
298.15	14.43	12.36	7.19
Lithium Metasilicate			
30	0.220	0.073	0.057
40	0.740	0.203	0.158
50	1.46	0.442	0.344
60	2.34	0.785	0.602
80	4.35	1.73	1.28
100	6.60	2.94	2.12
120	8.91	4.35	3.06
140	11.18	5.89	4.06
160	13.30	7.53	5.08
180	15.30	9.21	6.11
200	17.09	10.92	7.12
220	18.73	12.62	8.10
240	20.19	14.32	9.05
260	21.49	15.98	9.96
280	22.68	17.62	10.82
298.15	23.68	19.08	11.58
Magnesium Sulfide			
15	0.029	0.010	0.007
20	0.068	0.023	0.015
25	0.133	0.045	0.032
30	0.229	0.076	0.057
40	0.656	0.195	0.148
50	1.31	0.409	0.312
60	2.14	0.721	0.548
70	2.99	1.12	0.837
80	3.87	1.57	1.16
100	5.42	2.61	1.86
120	6.67	3.71	2.56
140	7.67	4.82	3.22
160	8.46	5.89	3.83
180	9.10	6.93	4.38
200	9.59	7.91	4.88
220	9.98	8.85	5.32

Table I. (Continued)

T, ° K.	C_p	S	$\frac{H - Ho}{T}$
Magnesium Sulfide			
240	10.29	9.73	5.73
260	10.52	10.56	6.09
280	10.72	11.35	6.41
298.15	10.89	12.03	6.68
Magnesium Formate			
15	0.485	0.150	0.120
20	0.948	0.350	0.265
25	1.53	0.622	0.460
30	2.21	0.959	0.693
40	3.84	1.81	1.27
50	5.70	2.87	1.97
60	7.62	4.08	2.75
70	9.49	5.40	3.58
80	11.31	6.79	4.44
100	14.55	9.67	6.15
120	17.31	12.57	7.78
140	19.64	15.42	9.31
160	21.65	18.18	10.73
180	23.35	20.83	12.04
200	24.84	23.37	13.25
220	26.15	25.79	14.36
240	27.37	28.12	15.40
260	28.52	30.36	16.36
280	29.66	32.51	17.27
298.15	30.66	34.41	18.06
Phosphorus Pentoxide			
15	2.73	1.17	0.89
20	4.60	2.22	1.59
25	6.27	3.43	2.36
30	7.58	4.69	3.13
40	8.97	7.06	4.42
50	10.38	9.22	5.47
60	11.56	11.21	6.38
70	13.30	13.12	7.24
80	15.14	15.02	8.12
100	18.65	18.76	9.86
120	22.63	22.52	11.66
140	26.46	26.30	13.50
160	30.18	30.08	15.36
180	33.71	33.83	17.20
200	37.13	37.57	19.03
220	40.34	41.26	20.82
240	43.33	44.90	22.57
260	46.21	48.48	24.28
280	49.05	52.01	25.95
298.15	51.56	55.17	27.43
Boron Phosphate			
15	0.079	0.026	0.020
20	0.158	0.059	0.043
25	0.282	0.107	0.078
30	0.465	0.173	0.127
40	0.949	0.371	0.269
50	1.54	0.644	0.463
60	2.19	0.982	0.696
70	2.87	1.37	0.957
80	3.79	1.80	1.24
100	5.11	2.76	1.86
120	6.68	3.83	2.53
140	8.24	4.98	3.24
160	9.76	6.18	3.96
180	11.24	7.42	4.69
200	12.65	8.67	5.41
220	14.01	9.94	6.13
240	15.31	11.22	6.84
260	16.55	12.49	7.54
280	17.73	13.76	8.23
298.15	18.75	14.91	8.84
Stannous Sulfate			
15	0.932	0.339	0.253
20	1.71	0.710	0.517
25	2.61	1.19	0.843
30	3.62	1.75	1.22
40	5.73	3.09	2.09
50	7.51	4.56	3.00
60	9.10	6.08	3.89
70	10.41	7.58	4.73
80	11.65	9.05	5.52
100	13.65	11.88	6.96
120	15.31	14.52	8.22
140	16.77	16.99	9.33
160	18.25	19.32	10.35
180	19.92	21.58	11.33
200	21.11	23.74	12.25
220	22.25	25.80	13.11
240	23.27	27.78	13.91
260	24.23	29.68	14.67
280	25.17	31.51	15.38
298.15	26.00	33.12	16.00
Sodium Fluosilicate			
15	0.75	0.262	0.193
20	1.67	0.595	0.440
25	2.76	1.08	0.792
30	3.98	1.69	1.22
40	6.36	3.16	2.21
Sodium Fluosilicate			
50	8.77	4.84	3.28
60	11.15	6.65	4.39
70	13.47	8.54	5.53
80	15.70	10.49	6.66
100	19.75	14.44	8.88
120	23.47	18.37	11.00
140	26.92	22.25	13.04
160	30.08	26.06	14.97
180	32.92	29.77	16.81
200	35.38	33.36	18.55
220	37.70	36.84	20.18
240	39.89	40.22	21.74
250	40.91	41.87	22.48
255	41.44	42.68	22.85
260	42.16	43.50	23.21
265	43.10	44.31	23.58
270	43.88	45.12	23.95
275	44.25	45.93	24.32
276	44.12	46.09	24.39
277	43.93	46.25	24.46
278	43.62	46.41	24.53
279	43.36	46.57	24.60
280	43.37	46.72	24.66
290	44.11	48.26	25.32
298.15	44.71	49.49	25.84
Aluminum Chloride Hexahydrate			
16	1.73	0.69	0.50
20	2.88	1.19	0.86
25	4.85	2.03	1.45
30	6.60	3.07	2.16
40	10.44	5.49	3.75
50	14.21	8.23	5.47
60	17.68	11.13	7.22
70	20.94	14.10	8.95
80	24.02	17.10	10.64
100	29.79	23.09	13.90
120	34.92	28.99	16.99
140	39.78	34.73	19.89
160	44.48	40.36	22.68
180	49.18	45.86	25.36
200	53.48	51.27	27.96
220	57.45	56.56	30.46
240	61.20	61.72	32.87
260	64.71	66.76	35.18
280	67.95	71.67	37.41
298.15	70.79	76.03	39.36

DISCUSSION

Shirley (*12*) reported heat capacity data on LiCl which are in good agreement with the present work over most of the temperature range studied. The calculated entropy at 298.15° K. given by Shirley is 14.17 gibbs per mole compared to 14.19 given here. Furukawa *et al.* (*4*) published data for KBH_4 which again are in reasonable agreement with the present work; our entropy at 298.15° K. is 25.55 gibbs per mole compared to 25.40 derived by Furukawa *et al.* The temperature and enthalpy of transition reported by Furukawa *et al.*, 77.16° K. and 53.8 cal. per mole, are in good agreement with 77.0° K. and 52.8 cal. per mole found here.

Thermal data given here may differ from quoted preliminary values (*1, 6, 7, 9*) because of reassessment and recalculations. In particular, values for phosphorus pentoxide communicated to Andon *et al.* (*1*) were considerably in error due to use of an outdated empty calorimeter calibration. [This is also the reason for discrepancies between the data for aluminum chloride quoted by Kelley and King (*9*) and recent work of Justice (*8*)]. Based on comparison with literature values as well as intralaboratory checks, it is estimated that the third-law entropies at 298.15° K. reported here are accurate to at least 1%. Entropies of this accuracy are useful in thermodynamic calculations, as evidenced by comparison with estimates based on the tables of ionic contributions listed by Latimer (*10*). As shown in Table II, the average deviation is 10% and in only one case is the estimate within 1% of the measured entropy.

Table II. Measured and Estimated Entropies at 298.15° K. in Gibbs per Mole

Compound	S°_{298} Measured	S°_{298} Estimated	% Diff.
KOH	18.85	14.2	−24.7
K_2CO_3	37.17	33.6	−9.6
K_2SiO_3	34.93	35.2	0.8
LiCl	14.19	13.5	−4.9
Li_2SiO_3	19.08	23.8	24.7
MgS	12.03	12.6	4.7
$SnSO_4$	33.12	30.3	−8.5
$AlCl_3 \cdot 6H_2O$	76.03	82.5	8.5

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Volumetric Behavior of a Polar-Nonpolar Gas Mixture: Trifluoromethane-Tetrafluoromethane System

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Compressibility factors were determined for the polar-nonpolar gaseous system, $CF_3H—CF_4$, for six compositions at temperatures between −30° and 95° C., and at temperatures as low as −70° C. for CF_4. The data extend to pressures as high as 1238 p.s.i.a. and are accurate to better than one part per thousand. Values are given for the constants in the Martin-Hou equation of state which correlate the volumetric data with average deviations of less than 0.5% for the pure components and 1.1% for the mixtures. Second and third virial coefficients were determined from the data; the virial coefficients for the pure gases and the interaction virial coefficients are presented. Intermolecular-potential-function parameters are given for CF_4, which correlate the second virial coefficient for this gas within its experimental uncertainty between −70° and 500° C.

THE APPARENT NEED for volumetric data on gas mixtures containing polar components, as well as a need for such data to interpret some vapor-liquid equilibrium data (*12*), prompted the determination of the volumetric behavior of the $CF_3H—CF_4$ system. Of the available methods of volumetric measurement, the Burnett method was selected as having the best combination of accuracy and efficiency.

The Burnett method is an isothermal experiment in which successive portions of a test gas, confined in a primary chamber, are allowed to expand into a secondary chamber, which is discharged and evacuated after each expansion. For each expansion, comparison of the ratio of the pressures before and after the expansion to the known volume ratio of the two chambers indicates the nonideality of the test gas. The Burnett method has been described in detail (*1, 13*).

EXPERIMENTAL

The experimental pressures were measured by balancing a hydraulic pressure generated by a dead-weight gage against the test-gas pressure, using a sensitive differential-pressure transducer (DP-cell). The latter employed a thin metallic diaphragm, the position of which was sensed by a magnetic-reluctance circuit. The pressure-measurement system had a sensitivity of 0.001 p.s.i. and an over-all accuracy of 0.01 p.s.i. The test-gas pressure was continually monitored on a recorder, except during and immediately following expansions, as a check for leaks and as evidence of the restoration of thermal equilibrium after each expansion.

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