Figure 1. Vapor pressure of di-*tert*-butyl peroxide: (*) experimental points, (+) calculated least-squares best fit line with $r^2 = 0.996$.

and ± 0.01 Torr for greater than 11.500 Torr). Temperature was measured with a chromel–alumel thermocouple resting in the liquid of the constant-temperature bath. The thermocouple was attached to a strip chart recorder and the pressure measurement was taken approximately 15 min after there was no detectable temperature change.

Results

The vapor pressure data are shown in Table I. The integrated

Clausius–Clapeyron equation (*1*) relates vapor pressure to temperature

$$\ln P = (-\Delta H_v/R)(1/T) + \text{constant} \qquad (1)$$

where P is the pressure, T the temperature in Kelvin, R the universal gas constant, and ΔH_v the molar heat of vaporization. The value of the constant depends in part on the units used for the pressure. The experimental values were fitted to eq 1 using the method of least squares. The best fit line is

$$\ln P = (-3.842 \times 10^3)(1/T) + 1.630 \times 10^1 \qquad (2)$$

where P is in Torr. Equation 2 or the vapor pressure curve in Figure 1 can be used to obtain vapor pressures to assist in the design of experiments. The coefficient of determination for the calculated line is 0.996. The calculated molar heat of vaporization is 7.63 kcal.

Literature Cited

(1) Barrow, G., "Physical Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1966, p 523.
(2) Benson, S. W., "The Foundations of Chemical Kinetics", McGraw-Hill, New York, N.Y., 1960, p 363.
(3) Milas, N. A., Surgenor, D. M., *J. Am. Chem. Soc.*, **68**, 205 (1946).
(4) Rieche, A., Brumshagen, W., *Ber. Dtsch. Chem. Ges.*, **61**, 951 (1928).
(5) Tobolsky, A. V., Mesrobian, R. B., "Organic Peroxides", Wiley, New York, N.Y., 1954, p 20.
(6) Williams, F. W., Sheinson, R. S., Bogan, D. J., Rabitz, H. A., Indritz, D., "Mechanistic Investigation of the Oxidative and Thermal Decomposition of Di-*tert*-Butyl Peroxide: An Experimental and Modeling Study", Presented at the Eastern States Section, Combustion Institute, Nov 1976.

Pressure–Temperature Relationship for Decomposition of Sodium Bicarbonate from 200 to 600 °F

Charles C. Templeton

Bellaire Research Center, Shell Development Company, Houston, Texas 77001

The equilibrium dissociation pressure of initially dry sodium bicarbonate (nahcolite) was experimentally determined between 200 and 600 °F. It was found necessary to use a constant ratio of initial gas volume to solid nahcolite volume, V_g/V_s, to obtain a unique pressure–temperature curve. Such pressure–temperature relationships were measured for three values of V_g/V_s, each curve showing three points of discontinuous slope. For $V_g/V_s = 1$, the pressure exceeded 6000 psia above 487 °F. Since the Green River oil shale formation in Colorado contains both beds and isolated nodules of nahcolite, the pressure developed by heating nahcolite may be a factor in developing porosity and permeability during an in situ thermal process for producing shale oil.

The Green River oil shale formation in the Piceance Basin, Colo., contains both layers and isolated nodules of nearly pure nahcolite (sodium bicarbonate) at depths between 1500 and 2300 ft. The dissolving of the layered nahcolite with warm water is a feature of planned in situ shale oil recovery processes de-

signed to create initial porosity. As a cavity wall is heated in the leaching and rubbling phase of the process, sealed-off nahcolite nodules will be heated and will develop a dissociation pressure due to the tendency to evolve carbon dioxide and water vapor. At high enough temperatures this pressure should become large enough to cause the nodules to "pop", thus causing cracking or rubbling of the cavity wall. This overall phenomenon could then be a mechanism for cavity growth.

The most complete set of decomposition pressures and temperatures of sodium bicarbonate available appears to be that of Caven and Sand (*2*) who made measurements between 86 and 230 °F. Within this temperature range the molar amounts of water and carbon dioxide evolved were equal; thus the decomposition under these conditions is represented by the reaction

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g) \qquad (1)$$
$$\text{nahcolite} \qquad \text{soda ash}$$
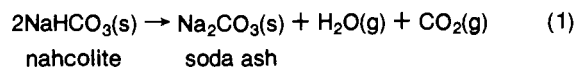
Thus no water condensed or formed solid hydrates. They reported their smoothed data as the equation

$$\log p = 11.8185 - (3340/T) \tag{2}$$

where p is expressed in millimeters of mercury and T is expressed on the Kelvin scale. This expression yields a representative value of 0.968 atm or 14.2 psi at 212 °F.

The literature contains no previous study, at pressures above 30 psi, of the decomposition of $NaHCO_3$ in a closed system. Previous studies in both open and closed systems in this low-pressure region have been summarized by Barrall and Rogers (*1*) who have made the most recent study in a closed system with differential thermal analysis (DTA) techniques. Their small DTA cell (0.8 mL in volume) kept the evolved gases in contact with the solids at a constant pressure of about 1 atm by allowing gas to expand but not escape. Under these conditions $NaHCO_3$ showed two decomposition endotherms, at 253 and 269 °F, with the maximum temperature of their DTA run being about 356 °F.

Barrall and Rogers state that the decomposition of $NaHCO_3$ in a closed system is a complex reaction series, rather than occurring in one step as indicated by eq 1. This is due to reaction occurring between undecomposed $NaHCO_3$ and its decomposition products when the gaseous products are retained in contact with the decomposing solid. True equilibrium requires time for slow reactions to occur; thus their DTA heating period of about 30–60 min may not be sufficient for equilibrium to be attained. They conclude that, in their closed system, the decomposition starts as indicated by reaction 1. After sufficient products have been formed, wegscheiderite is produced

$$3NaHCO_3(s) + Na_2CO_3(s) \rightarrow Na_2CO_3 \cdot 3NaHCO_3(s) \tag{3}$$

nahcolite   soda ash   wegscheiderite
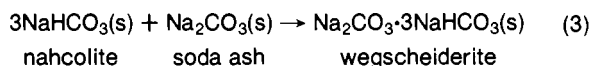
They state that water vapor must be present for wegscheiderite to form, even though water does not participate in reaction 3. Apparently the combination of eq 2 and 3 corresponds to their 253 °F endotherm, while the 269 °F endotherm corresponds to the completion of decomposition

$$2(Na_2CO_3 \cdot 3NaHCO_3)(s)$$

wegscheiderite

$$\rightarrow 5Na_2CO_3(s) + 3CO_2(g) + 3H_2O(g) \tag{4}$$

soda ash
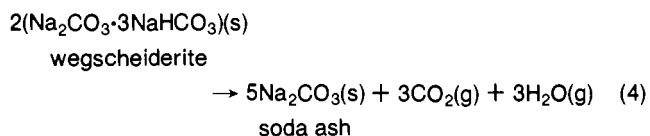
Other solid intermediates that may occur are trona, $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$, and thermonatrite, $Na_2CO_3 \cdot H_2O$.

Our practical aim in this study was to gather pressure–temperature data which, firstly, might apply to a pure nahcolite nodule contained within an impervious oil shale matrix with no gas space and, secondly, to subsequent situations in which some carbon dioxide and water vapor have escaped into a definite gas-filled volume within the oil shale matrix and is still in contact with a nahcolite nodule.

Experimental Methods

The experimental setup is shown in Figure 1. A given weight of reagent grade $NaHCO_3$ (J. T. Baker Chemical Co.) is placed inside a stainless steel pressure bomb (about 300 mL in volume) which in turn is placed in a constant-temperature oven (whose temperature was measured with a thermocouple). The bomb is connected to an external pressure gauge through tubing containing a silicone fluid (Dow-Corning 200) in all regions that may be cooler than oven temperature; in this way the nahcolite and evolved gases are kept at the oven temperature. At the start of each run the bomb system containing air at ambient conditions is closed and the oven is brought to the desired temperature over about 2 h. A constant gauge pressure is observed after 24–48 h of equilibration. A gauge pressure, p_{run}, is higher than the dissociation pressure, p, due to two reasons; the "inert" air pressure has increased due to heating, and the silicone obviously exerts some vapor pressure of its own at oven temperature. A blank pressure, p_B, to compensate for these two effects at a
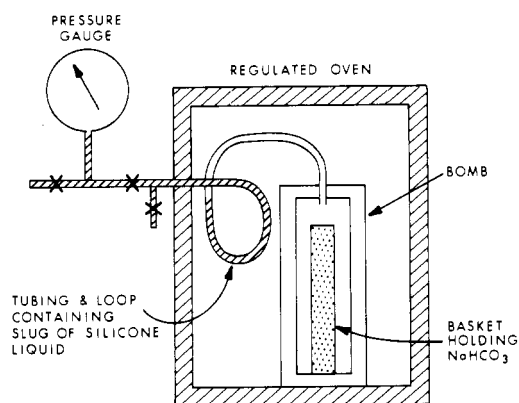

Figure 1. Schematic of apparatus used for determining pressure–temperature curve for sodium bicarbonate.

given temperature was determined by replacing the basket with a steel cylinder. The p_B values thus obtained as a function of temperature gave a straight line when plotted in log p_B vs. $(1/T,$ K). A representative value of p_B was 16 psi at 400 °F, which is about 2% of the observed p_{run} at 400 °F. Finally we have taken the absolute value of p at a given temperature as the difference between the corresponding gauge pressures; i.e., $(p_{run} - p_B)$.

As indicated above the routine practice was to approach equilibrium from below by raising the temperature. One attempt was made to reach equilibrium from above. During run 1, after the (353 °F, 676 psi) and (366 °F, 750 psi) points had been taken from below, the temperature was again lowered to 353 °F. After 72 h the pressure $(p_{run} - p_B)$ had fallen to 710 psi. Apparently the system approached equilibrium more slowly from above than from below. Thus we decided to continue making the measurements from below, realizing that the results might be slightly too low.

It was necessary to make runs at several ratios of initial bomb gas volume (V_g) to initial solid nahcolite volume (V_s) to ascertain whether the relative volume of the phases was a "degree of freedom" in the sense of the phase rule. To calculate V_g/V_s, V_s was determined by dividing the initial weight of nahcolite in grams by its grain density, 2.16 g/cm^3. The total internal volume of the system was obtained from its measured dimensions. Finally V_g was taken as the total internal volume less V_s. Thus an initial value of V_g/V_s at room temperature was obtained. No correction of V_g/V_s for expansion of the system with temperature was made.

Results

Four runs (1–4) were made for $V_g/V_s = 4.02$; this involved placing about 127 g of nahcolite in the basket within the bomb. Two runs (5 and 6) were performed for $V_g/V_s = 1.59$; for this about 252 g of nahcolite was placed in the bomb (without the basket), filling the bomb to within 0.5 in. of the top. One run (7) was carried out for $V_g/V_s = 1.00$; in this case the bomb was filled as full as possible with nahcolite. The value of $V_g/V_s = 1.00$ is about the minimum that can be attained, since the powdered nahcolite has a porosity of 45–50%. The (p, T) data for all the runs are listed in Table I and are plotted on a linear scale in Figure 2.

The points for the four runs having $V_g/V_s = 4.02$ overlap in Figure 2 and define a single (p, T) relationship within the accuracy of the pressure readings. This reproducibility leaves little doubt that equilibrium from below has been obtained. The curve drawn through the $V_g/V_s = 4.02$ points is seen to have four separate segments defining three discontinuities in slope. Similar curves have been drawn for the two runs with $V_g/V_s = 1.59$ and for the single run at $V_g/V_s = 1.00$. It is apparent that some volume parameter (such as V_g/V_s) must be specified to define a single

**Table I. Experimental Pressure–Temperature Data for Nahcolite Decomposition**

	Temp, °F	Total pressure, psia
Run 1 (V_g/V_s = 4.02)	225	18.7
	256	48.3
	295	139
	323	300
	353	676
	366	750
	383	790
	413	888
	443	1732
	455	1896
	469	1990
	487	2125
Run 2 (V_g/V_s = 4.02)	418	933
	431	1297
	442	1668
Run 3 (V_g/V_s = 4.02)	515	2398
	533	2572
	560	2861
	582	3110
	606	3274
Run 4 (V_g/V_s = 4.02)	320	275
	341	476
	360	748
	380	805
	400	864
Run 5 (V_g/V_s = 1.59)	425	1868
	438	1942
	460	2940
	466	3540
Run 6 (V_g/V_s = 1.59)	302	173
	351	631
	401	1714
	410	1753
	451	2320
	462	3310
	473	3965
	482	4060
	493	4204
	504	4330
	513	4450
	529	4660
	543	4860
	561	5140
Run 7 (V_g/V_s = 1.0)	300	173
	320	315
	338	522
	356	876
	378	1625
	399	2460
	419	2590
	430	2660
	439	2720
	451	2810
	462	3060
	473	4440
	487	6060
	495	6160
	504	6330

(p, T) relationship. Thus volume ratio, in addition to temperature, is a degree of freedom in this system.

The points of slope discontinuity have been labeled P_1, P_2, and P_3 in order of increasing temperature. The p and T values for each slope discontinuity have been read from Figure 2 and are recorded in Table II.

Discussion

Phase Rule Considerations. Only at temperatures below the first slope discontinuity can the system be regarded as two
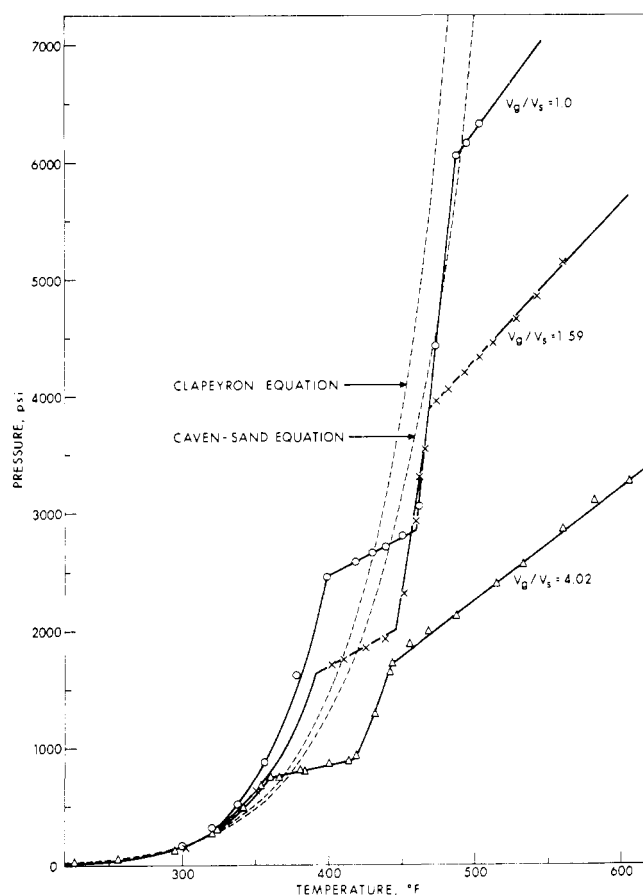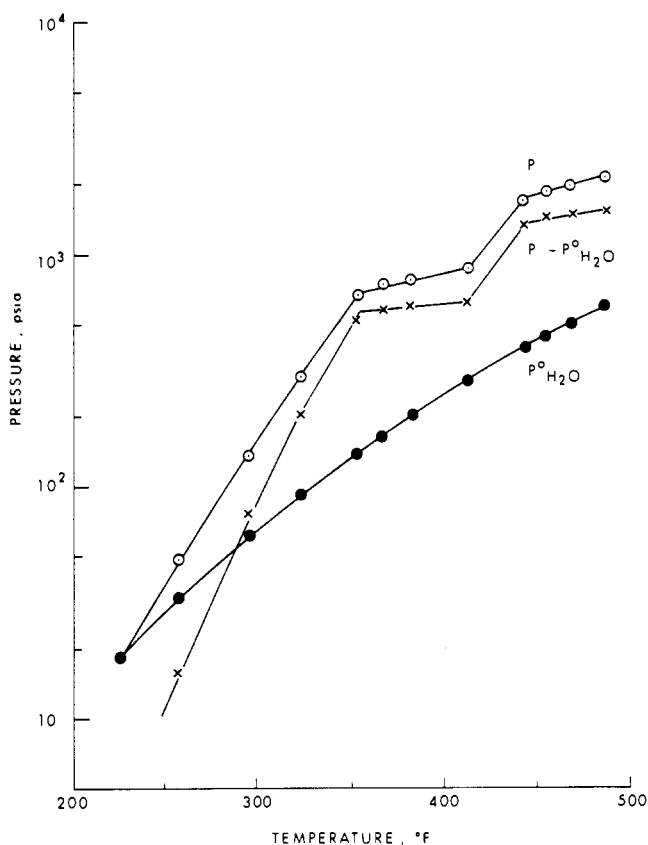

Figure 2. Pressure–temperature data for various values of V_g/V_s compared with Caven–Sand equation and Clapeyron equation.

components corresponding to the nahcolite decomposition to soda ash of eq 1 with the molar amounts of water and carbon dioxide in the gas phase being equal. For the two-component case ($C = 2$) with two solid phases and one gas phase ($P = 3$), there is only one degree of freedom ($F = 2 - 3 + 2 = 1$) and fixing the temperature alone should fix the pressure. However, at higher temperatures with the carbon dioxide and water partial pressures not equal (for whatever reaction) there are three components, which is also the maximum number for this system. Then for two solid phases and one gas phase, there are two degrees of freedom ($F = 3 - 3 + 2 = 2$) and both the temperature and some volume parameter must be fixed to fix the pressure. This latter analysis could apply to a solid–liquid–gas system as well as to the above solid–solid–gas system and either might apply to any of the three segments of our (p, T) plots above P_1.

Figure 3 illustrates an argument based on the data of run 1 which indicates that the partial pressures of CO_2 and H_2O cannot be equal at higher temperatures, and hence the system must then have three components. The experimental pressure, p, has been plotted vs. temperature. Next literature values (4) of the vapor pressure of pure water, $P^0_{H_2O}$, have been plotted; these should represent the maximum level of the actual vapor pressure of water in our system. Finally the difference, $p - p^0_{H_2O}$, should approximate the partial pressure of carbon dioxide. Above 350 °F, $p - p^0_{H_2O}$ is greater than $P^0_{H_2O}$ by a factor of 2 or more. Thus at higher temperatures some water must either condense or react with the solids to form hydrates such as thermonatrite, $Na_2CO_3 \cdot H_2O$. Even though Caven and Sand (2) did not observe the four-phase system, $NaHCO_3–Na_2CO_3–Na_2CO_3 \cdot H_2O$–vapor, as resulting from decomposition of $NaHCO_3$ below 230 °F, they did calculate the equilibrium pressure of this four-phase system from the (p, T) relationships for $NaHCO_3$ and $Na_2CO_3 \cdot H_2O$. If the present study had not found the apparent dependence of the (p, T)

Table II. Pressure–Temperature Data for Slope Discontinuities

V_g/V_s	Total pressure, psia	Temp, °F
	First Discontinuity (P_1)	
4.02	750	360
1.59	1610	388
1.00	2450	399
0.00	4437	421
	Second Discontinuity (P_2)	
4.02	900	419
1.59	2000	446
1.00	2850	460
0.00	4810	490
	Third Discontinuity (P_3)	
4.02	1700	442
1.59	3900	469
1.00	6050	487
0.00	11140	528

Figure 3. Pressure–temperature data for run 1.

curves on V_g/V_s, such a solid–solid–solid–vapor system would have been a simple explanation of a single (p, T) relationship above 350 °F.

A few attempts were made to identify the solid or liquid phases that existed in the system with quenching experiments. A small cell built from 0.24-in. o.d. stainless steel tubing and Swagelock end plugs was filled with nahcolite and heated in an oven. It was removed after 24 h or more and plunged into an ice water mixture. Within 30 s after quenching, one end plug was removed to release the H_2O–CO_2 gas phase, and the solids were submitted for x-ray diffraction analysis.

A sample quench from 500 °F was found by x-ray diffraction to contain soda ash (Na_2CO_3), 20%; trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$), 15%; wegscheiderite ($Na_2CO_3 \cdot 3NaHCO_3$), 10%; thermonatrite ($Na_2CO_3 \cdot H_2O$), 20%; and nahcolite ($NaHCO_3$), 35%. These results were typical of all our quenching experiments

starting with only $NaHCO_3$. Since no more than three solid phases were expected, it was concluded that extra phases formed as the system cooled. Thus experimental identification of the solid phases involved in each segment of the (p, T) plots was not obtained.

The region at temperatures above P_3 for any of our runs may have a "stoichiometric" explanation; i.e., no $NaHCO_3$ remains in the solid phases either as such or as an addition compound with Na_2CO_3. Thus one could propose that above P_3 the solid phase is pure Na_2CO_3, together with a liquid phase and a gas phase. With such a model, and with several assumptions, it is possible to roughly calculate the final branch of the curve for each V_g/V_s value. Because of its conjectural nature this discussion is included in the supplementary material.

The Clapeyron Equation and the Region below P_1. These (p, T) data for nahcolite decomposition should agree with the Claypeyron equation if all the pertinent thermodynamic data are available and the correct pressure-generating reaction is chosen for a given segment of a (p, T) curve. The Clapeyron equation is

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} = \frac{\Delta H}{T(\Delta V_{gas} + \Delta V_{solids})} \tag{5}$$

where ΔH and ΔV are, respectively, the changes in enthalpy and volume for the reaction. (If p is expressed in atmospheres, T as K, and V in liters, ΔH must be expressed in L atm. ΔH(L atm) = $(0.04129)\Delta H$(cal).) Thus one needs ΔH and solid densities as a function of temperature, as well as the gas law (or a real gas equation) to proceed.

Such data are available only for the decomposition of nahcolite to soda ash described by eq 1. Even for this reaction only the enthalpy change is known as a function of temperature; the volume change is only known at 25 °C. From literature sources (5) we have $\Delta H_{298.1} = 30.85$ kcal/mol, $\Delta C_p = 1.42$ cal/(deg mol) and

$$\Delta H_T = 30850.0 + 1.42(T - 298.1), \text{ cal/mol} \tag{6}$$

At 77 °F the density (3) of $NaHCO_3$ is 2.16 g/cm³ and that of Na_2CO_3 is 2.53 g/cm³, from which a ΔV_{solids} value of 35.87 cm³ can be calculated. Because no other data are available this ΔV_{solids} value will be assumed to be constant with temperature. Since $\Delta V_{gas} = 2RT/p$, substituting in eq 5 yields

$$\frac{dp}{dT} = (0.04129) \frac{[30850.0 + (1.42)(T - 298.1)]}{T[(0.1642T/P) - 0.03587]} \tag{7}$$

where p is expressed as atmospheres and T as K. Equation 7 cannot be integrated analytically, but (p, T) data may be obtained by numerical integration, based on an initial value of 0.968 atm at 212 °F from Caven and Sand. This calculated Clapeyron curve, along with the Caven and Sand relationship of eq 2, has been plotted in Figure 2. The Clapeyron curve is seen to give higher pressures than the Caven–Sand curve and both give lower pressures than our experimental curves below the first slope discontinuity P_1. The apparent dependence of the curves on V_g/V_s as P_1 is approached (especially for the $V_g/V_s = 1.0$ curve) is surprising. No adequate explanation of these deviations is in hand, yet we have little alternative to believing that $NaHCO_3$ decomposes directly to Na_2CO_3 according to eq 1 up to P_1.

Direct Extrapolation to Obtain a $V_g/V_s = 0$ Curve. The ultimate measure of the pressure available for rubbling is the (p, T) relationship for an isolated nahcolite nodule within a shale matrix which has no gas volume and from which no gas can escape until rubbling breakdown occurs. This would correspond to $V_g/V_s = 0$. We cannot realize this condition in our apparatus with powdered nahcolite, even if we pack the bomb full, because the nahcolite has considerable porosity. (A low value of V_g/V_s could be attained by placing a close-fitted cylinder of natural dense nahcolite within a metal bomb but this was ruled out for safety reasons.) We may, as an alternative, extrapolate our data as a

Table III. *P–T* **Points Read from** V_g/V_s = 0.00 **Curve**

Temp, °F	Total pressure, psia	Temp, °F	Total pressure, psia
300	300	440	4510
310	365	450	4565
320	450	460	4625
330	560	470	4680
340	680	480	4740
350	860	490	4810 (P_2)
360	1090	500	6050
370	1400	510	7575
380	1780	520	9400
390	2220	528	11140 (P_3)
400	2750	540	11350
410	3425	550	11520
421	4437 (P_1)	560	11710
430	4460	570	11900

function of V_g/V_s to the limit of V_g/V_s = 0. Such V_g/V_s = 0 data, together with our experimental data, would allow us to estimate (p,T) data for intermediate values of V_g/V_s which might pertain to a given nodule-crack system. However, this direct extrapolation scheme is arbitrary and empirical having no real theoretical basis; it was attempted only for the purpose of making plausible predictions about rubbling of oil shale.

The slope discontinuities are the best features of our p,T curves to be extrapolated to V_g/V_s = 0. The data for each slope discontinuity have been fitted to the following parabolic expressions

$$P = P_0 + a(V_g/V_s) + b(V_g/V_s)^2 \qquad (8)$$

and

$$T = T_0 + m(V_g/V_s) + n(V_g/V_s)^2 \qquad (9)$$

For V_g/V_s = 0, P_0 and T_0 are the coordinates of the slope discontinuity in question; these have been recorded in Table II.

A p,T curve for V_g/V_s = 0 was constructed as follows. First the coordinates of the three-slope discontinuities were plotted. Between P_1 and P_2 and between P_2 and P_3 slightly curved lines were drawn similar to the segment shapes in Figure 2. Below P_1 and above P_3 the curve was drawn to be similar to the curve

for V_g/V_s = 1.00. Table III contains p,T points read from the V_g/V_s = 0 curve at approximately 10 °F intervals.

The "Popcorn" Mechanism of Rubbling in In situ Shale Oil Processes. During the leaching and rubbling phase of an in situ oil shale process, there will be a portion of oil shale near a cavity boundary that will be heated by conduction in a dry state. If such a dry-heated portion contains an enclosed nahcolite nodule, it should develop an excess internal pressure that might be relieved by breaking loose a piece of shale that would expose the nodule or develop cracks that would allow gas to escape into the cavity. In addition existing cracks in the shale matrix connecting the nodule and the cavity wall might be enlarged. Whereas with a completely sealed-off nodule the pressure should rise monotonically with increasing temperature leading to an instantaneous breaking of the matrix, with the crack-connected nodule there would be a competition between pressure rise with temperature and the loss of gas through the cracks. Both of these cases are included within the concept of the "popcorn" mechanism or rubbling.

Comparison of the V_g/V_s = 0 data in Table III with the experimental curves in Figure 2 provides a basis for interpolating a value of the pressure for any value of V_g/V_s < 4.02 at a given temperature. In particular the data of Table III may be used for a completely isolated nodule (no gas space). Above 400 °F the whole range of pressures is probably high enough to cause some rubbling in view of the fact that rock under tensile stress is not strong. Hence the present work is encouraging in relation to the existence of "popcorn" rubbling in in situ shale oil recovery processes.

Literature Cited

(1) Barrall, E. M., Rogers, L. B., *J. Inorg. Nucl. Chem.*, **48**, 41 (1966).
(2) Caven, R. M., Sand, H. J. S., *J. Chem. Soc.*, **99**, 1359 (1911).
(3) Gmelin Handbook, 8 Auflage, Natrium Ergunzungsband, Lieferung 3, Verlag-Chemie, Weinheim/Bergstr., 1966.
(4) Keenan, J. H., Keys, F. G., Hill, P. G., Moore, J. G., "Steam Tables Thermodynamic Properties of Water Including Vapor, Liquid and Solid Phases", Wiley, New York, N.Y., 1969.
(5) Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., Jaffe, I., U.S. *Natl. Bur. Stand. (U.S.), Circ.*, **No. 500** (1952).