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The Anthracite Smokers of Eastern Pennsylvania: $P_{S_2(g)}$-T Stability Diagram by TL Analysis[1]

Glenn B. Stracher[2]

Coal seams and culm banks associated with mine fires in the anthracite region of eastern Pennsylvania have been burning for decades. Many of the fires may have ignited by spontaneous combustion or by the burning of trash. Minerals associated with the combustion of anthracite form by the condensation of gas exhaled through surficial gas vents or "anthracite smokers." A Pressure-Temperature (P-T) stability diagram is constructed for the condensation of orthorhombic sulfur from anthracite gas using "Thermodynamic Loop Analysis" (TL analysis). This method of analyzing chemical systems incorporates Kirchhoff's Law into a four step procedure structured around a closed thermodynamic cycle or "thermodynamic loop." The four steps, referred to as "The Four S'S of Thermodynamic Loop Analysis," include: (1) "Set Up"—graphical characterization of the problem, (2) "Sum"—the application of thermodynamic principles, (3) "Substitute"—the use of materials data available from the literature, and (4) "Solve"—computation of one or more variables. The example presented demonstrates that thermodynamic loops can incorporate any number of polymorphic phase transformations. In addition, thermodynamic loop analysis is applicable to any geologic process involving the condensation of minerals from a gas. The stability diagram derived by TL analysis may have applicability in monitoring the release of sulfur gas into the atmosphere.

KEY WORDS: thermodynamic loop, thermodynamic loop analysis.

INTRODUCTION

Since the 1930s, many anthracite mines in eastern Pennsylvania have shut down with little or no effort made to remove culm banks (Lapham and others, 1980). Numerous fires, started in waste piles as well as anthracite seams, have been burning for decades.

Minerals, associated with the subsurface combustion of anthracite, form by the condensation of gas exhaled through surficial gas vents (Lapham and others, 1980; Stracher, 1993) or *anthracite smokers*. The exhalation-condensation process is analogous to the way in which some minerals form in fumarolic

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[1] Received 31 October 1994; accepted 26 January 1995.

[2] Department of Science and Mathematics, University System of Georgia, East Georgia College, Swainsboro, Georgia 30401.

or solfatara environments (Stoiber and Rose, 1974). Mineral condensates include sulfur (S), downeyite (SeO_2), orpiment (As_2S_3), laphamite ($As_2(Se,S)_3$), salammoniac (NH_4Cl), gypsum ($CaSO_4 \cdot H_2O$), and mullite ($Al_6Si_2O_{13}$). Finkelman and Mrose (1977), Lapham and others (1980), Dunn and others (1986), and Stracher (1993) discuss these minerals and others associated with burning anthracite.

This paper presents a systematic thermodynamic procedure for constructing a stability diagram for the condensation of orthorhombic sulfur from anthracite gas. The technique is applicable to the condensation of minerals from gaseous exhalations associated with *any* geologic process and can incorporate any number of polymorphic phase transformations.

ANTHRACITE REGION: MINE RELATED FIRES

The anthracite region of eastern Pennsylvania is predominantly in the central Appalachian Mountain section of the Valley and Ridge Province. This region includes the Northern, Eastern Middle, Western Middle, and Southern Anthracite Fields shown in Figure 1. These fields are Pennsylvanian lithotectonic components of Appalachian Mountain synclinoria and anticlinoria (Wood and Bergin, 1970).

Of all the burning anthracite culm banks and mine fires reported by Lapham and others (1980), the Wanamie mine fire in Glen Lyon (Fig. 1) is the only one for which there is a known origin. The Wanamie fire started from downed electrical wires caused by a mine train accident in 1956. The origin of fire at all other locations is subject to conjecture. Possibilities include the burning of trash as well as spontaneous combustion resulting from hay, manure, and oil-soaked rags, or lumber in the anthracite waste piles (Jones and Scott, 1939). Limacher (1963) has suggested that spontaneous combustion might result from exothermic sulfide oxidation reactions associated with oxygen circulating through joints in coal seams. The United Verde mine fire of 1894 at Jerome, Arizona for example, presumably started from the spontaneous combustion of sulfide minerals exposed to air (Anthony, Williams, and Bideaux, 1977, p. 29). The Centralia mine fire (Fig. 1), burning since 1962, involves hundreds of acres beneath the town of Centralia (Geissinger, 1990). The fire may have started when a landfill in an abandoned strip mining cut was ignited to reduce its volume and control rodents (DeKok, 1986, p. 20). According to Geissinger (1990), the landfill fire possibly spread to and ignited a coal seam in the dump.

Anthracite fires can generate enormous amounts of heat. Lapham and others (1980) report subsurface borehole temperatures of 730°C at 11 meters near Glen Lyon and gas vent temperatures higher than 660°C at Forestville (Fig. 1).

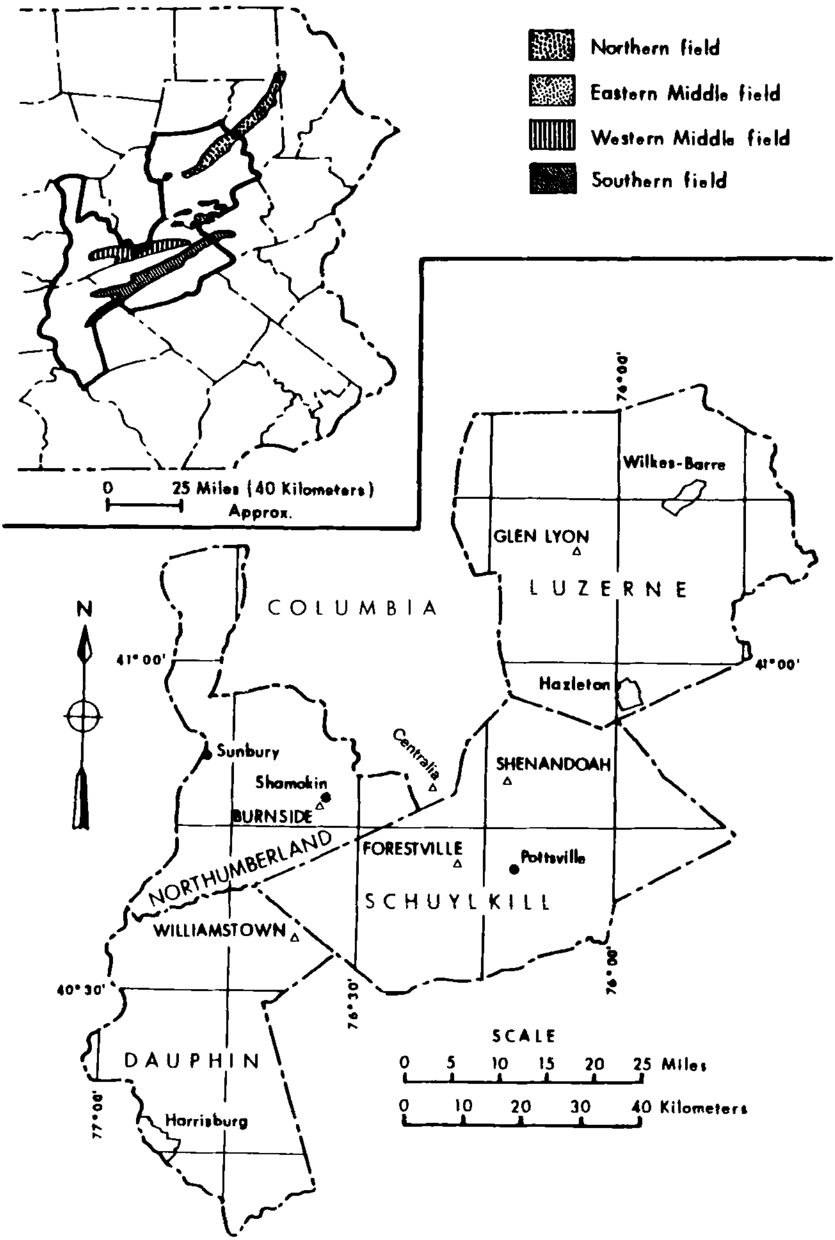


Figure 1. Map of eastern Pennsylvania illustrating four anthracite fields in Dauphin, Schuylkill, Luzern, and Northumberland Counties [modified from Lapham and others (1980) with permission of Pennsylvania Geological Survey]. Mine-related anthracite fires are designated by the symbol Δ.

THERMODYNAMICS OF VENTED GASES

Gas to Solid Phase Transformation

The process by which minerals condense *directly* from anthracite, volcanic, or other vented gases is a gas to solid phase transformation. Hence, condensation occurs when the vented gas is cooled below the gas–liquid transformation temperature. Surficially exhaled gases are cooled when they encounter *heat sinks* (Johnson and Stracher, 1994) such as the atmosphere, sediment, rocks, and large trees (Stracher, 1993).

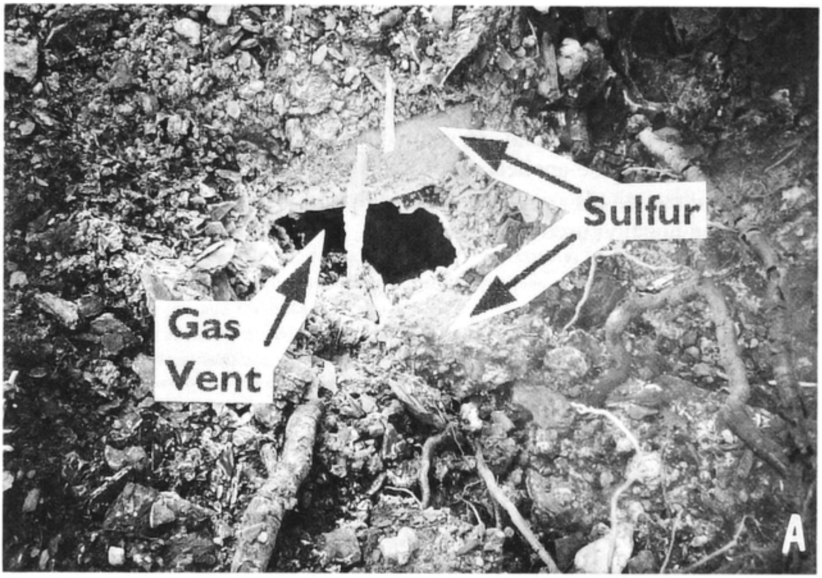
Thermodynamic Loop Analysis: Constructing a P-T Stability Diagram

The technique presented here for constructing a $P_{S_2}(g)$-T stability diagram for the transformation of anthracite gas to orthorhombic sulfur incorporates Kirchhoff's Law and a four step procedure structured around a closed thermodynamic cycle referred to as a *Thermodynamic Loop* or *TL* (terminology of Johnson and Stracher, 1994). The application of Kirchhoff's Law to such a cycle is termed *Thermodynamic Loop Analysis* or *TL analysis* (Johnson and Strachcr, 1994). The four step analytical procedure, termed *The Four S'S of Thermodynamic Loop Analysis* by Johnson and Stracher (1994), includes: (1) *Set Up*—graphical characterization of the problem with a thermodynamic loop, (2) *Sum*—the application of thermodynamic principles to the loop, (3) *Substitute*—the use of materials data available from the literature, and (4) *Solve*—computation of one or more loop variables.

Thermodynamic Loop Analysis: Anthracite Smokers and Sulfur

Sulfur is one of the more abundant mineral condensates associated with gaseous exhalations from anthracite smokers (Fig. 2). According to Lapham and others (1980), the stable polymorph of sulfur at room temperature, orthorhombic α-sulfur, usually condenses *directly* from anthracite gas. Some anthracite smokers exhale gas so slowly that the gas hovers about the vent before moving away from it as a slow-moving pocket of smoke (Fig. 2). Therefore, at least in some situations, it is reasonable to assume that the total pressure of the exhaled gas is one atmosphere or less. At this low pressure, gas behavior is *ideal* (Johnson and Stracher, 1994). Once the gas comes into contact with rock, sediment, or trees it cools and orthorhombic sulfur may condense. The thermodynamic problem for consideration thus can be phrased as follows:

> Construct a $P_{S_2}(g)$-T stability diagram for the condensation of anthracite gas to orthorhombic sulfur when the partial pressure of sulfur gas $P_{S_2}(g) < 1$ atm. Label the regions stable to sulfur gas and orthorhombic sulfur.



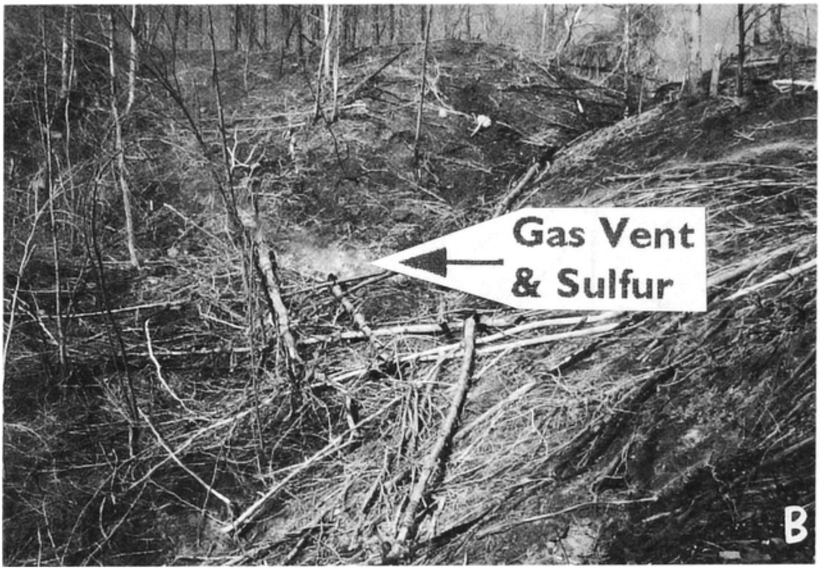


Figure 2. Gas vents or "anthracite smokers" at southern end of Centralia, Pennsylvania. A. Sulfur surrounding vent measuring 12 × 15 cm. Anthracite gas hovered about vent for about half-minute and then moved away as slow moving pocket of smoke. Several rock specimens collected near vent were so hot they burned through author's insulated gloves. B. Sulfur surrounding gas vent 20 meters immediately north of vent shown in A. All trees are dead and covered with a light coating of sulfur (not visible in photo). Field of view is approximately 35 meters.

Solution. A thermodynamic loop incorporating the necessary phase changes is "Set Up" in step 1 (Fig. 3). Cyclic changes are illustrated by *arbitrarily oriented* vertical and horizontal arrow directions. A counterclockwise summation direction is used for the application of Kirchhoff's Law. However, a clockwise summation direction also could be used (Johnson and Stracher, 1994). Table 1 describes the notation used in the loop.

(1) *Set up.*

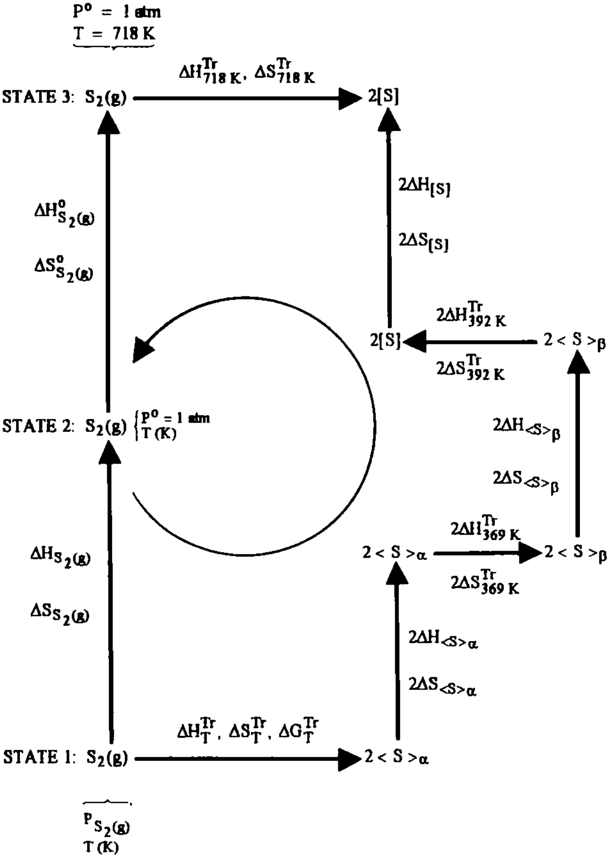


Figure 3. Thermodynamic loop for condensation of orthorhombic sulfur from anthracite gas. Note polymorphic changes in orthorhombic α- and monoclinic β-sulfur.

Table 1. Thermodynamic Loop Notation: Condensation of Orthorhombic Sulfur from Anthracite Gas

ΔH_T^{Tr}, ΔS_T^{Tr}, ΔG_T^{Tr} = Molar enthalpy, entropy, and Gibbs free energy of transformation, respectively, at temperature T.
$\Delta H^{\mathrm{o}}_{S_2(\mathrm{g})}$, $\Delta S^{\mathrm{o}}_{S_2(\mathrm{g})}$ = Standard molar enthalpy and entropy changes of diatomic sulfur gas, respectively.
$\Delta H_{S_2(\mathrm{g})}$, $\Delta S_{S_2(\mathrm{g})}$ = Molar enthalpy and entropy changes, respectively, of diatomic sulfur gas.
$\langle S\rangle_\alpha$, $\langle S\rangle_\beta$ = Orthorhombic and monoclinic sulfur polymorphs, respectively.
$S_2(\mathrm{g})$, $[S]$ = Sulfur gas and liquid sulfur, respectively.
P, T = Pressure in atmospheres (atm) and temperature in degrees Kelvin (K), respectively.
$^{\mathrm{o}}$ Superscript "o" designates *standard state* defined by $P^{\mathrm{o}} = 1$ atm.

(2) *Sum*. Kirchhoff's Law is applied by summing counterclockwise about the TL. Because enthalpy and entropy are *state functions*, they are path independent. Hence, their sums about the TL are zero (Johnson and Stracher, 1994) or

$$\Sigma\Delta H_{\mathrm{TL}} = 0 \text{ (enthalpy)} \qquad \Sigma\Delta S_{\mathrm{TL}} = 0 \text{ (entropy)} \tag{1}$$

$$\begin{aligned}\Sigma\Delta H_{\mathrm{TL}} &= 0 = \Delta H_T^{\mathrm{Tr}} + 2\Delta H_{\langle S\rangle\alpha} + 2\Delta H_{369\,\mathrm{K}}^{\mathrm{Tr}} + 2\Delta H_{\langle S\rangle\beta}\\ &\quad + 2\Delta H_{392\,\mathrm{K}}^{\mathrm{Tr}} + 2\Delta H_{[S]}\\ &\quad - \Delta H_{718\,\mathrm{K}}^{\mathrm{Tr}} - \Delta H^{\mathrm{o}}_{S_2(\mathrm{g})} - \Delta H_{S_2(\mathrm{g})}.\end{aligned}$$

$$\begin{aligned}\Sigma\Delta S_{\mathrm{TL}} &= 0 = \Delta S_T^{\mathrm{Tr}} + 2\Delta S_{\langle S\rangle\alpha} + 2\Delta S_{369\,\mathrm{K}}^{\mathrm{Tr}} + 2\Delta S_{\langle S\rangle\beta}\\ &\quad + 2\Delta S_{392\,\mathrm{K}}^{\mathrm{Tr}} + 2\Delta S_{[S]}\\ &\quad - \Delta S_{718\,\mathrm{K}}^{\mathrm{Tr}} - \Delta S^{\mathrm{o}}_{S_2(\mathrm{g})} - \Delta S_{S_2(\mathrm{g})}.\end{aligned}$$

(3) *Substitute*. TL variables are calculated using the thermodynamic data in Table 2 and the equations:

$$\Delta H = \int_{T_1}^{T_2} C_p \, dT \tag{2}$$

$$\Delta S = \int_{T_1}^{T_2} C_p \, dT/T \tag{3}$$

$$\Delta S_{\mathrm{T}}^{\mathrm{Tr}} = \Delta H_T^{\mathrm{Tr}}/T \tag{4}$$

ΔH and ΔS are molar enthalpy and entropy changes, respectively, from temperature T_1 to T_2 for a substance with constant pressure molar heat capacity,

Table 2. Thermodynamic Data from Weast and others (1989)[a]

(1) Sulfur Enthalpies of Transformation, ΔH^{Tr} (J/mol), where J = joules:

(a) $\underbrace{\langle S\rangle_{\alpha}}_{\text{Orthorhombic}} \rightarrow \underbrace{\langle S\rangle_{\beta}}_{\text{Monoclinic}}$: $\Delta H^{\mathrm{Tr}}_{369\,\mathrm{K}} = 368$ (b) $\underbrace{\langle S\rangle_{\beta}}_{\text{Monoclinic}} \rightarrow \underbrace{[S]}_{\text{Liquid}}$: $\Delta H^{\mathrm{Tr}}_{392\,\mathrm{K}} = 1226$

(c) $\underbrace{S_2(g)}_{\text{Gas}} \rightarrow \underbrace{2[S]}_{\text{Liquid}}$: $\Delta H^{\mathrm{Tr}}_{718\,\mathrm{K}} = -20{,}920$

(2) Sulfur Heat Capacities, Cp [J/(mol · K)], where J = joules:

(a) $C_p^{\langle S\rangle_\alpha} = 14.98 + 26.12 \times 10^{-3}T$ (b) $C_p^{\langle S\rangle_\beta} = 14.90 + 29.08 \times 10^{-3}T$

(c) $C_p^{[S]} = 22.59 + 20.92 \times 10^{-3}T$

[a] Data from Weast and others (1989, p. D-45) has been converted to SI units for this paper.

C_p, ΔS_T^{Tr} and ΔH_T^{Tr} are molar entropy and enthalpy changes, respectively, for a phase transformation at temperature T.

From Equations (2), (3), and (4):

$$\text{(a)}\ 2\Delta H_{\langle S\rangle\alpha}(J) = \int_T^{369} 2C_P^{\langle S\rangle\alpha}\,dT = 14{,}612 - 29.96\mathrm{T} - 26.12 \times 10^{-3}T^2.$$

$$2\Delta S_{\langle S\rangle\alpha}(J/K) = \int_T^{369} 2C_P^{\langle S\rangle\alpha}\,dT/T$$

$$= 196.36 - 29.96\ln(T) - 52.24 \times 10^{-3}T.$$

$$\text{(b)}\ 2\Delta H_{\langle S\rangle\beta}(J) = \int_{369}^{392} 2C_P^{\langle S\rangle\beta}\,dT = 1{,}194.4.$$

$$2\Delta S_{\langle S\rangle\beta}(J/K) = \int_{369}^{392} 2C_P^{\langle S\rangle\beta}\,dT/T = 3.14.$$

$$\text{(c)}\ 2\Delta H_{[S]}(J) = \int_{392}^{718} 2C_P^{[S]}\,dT = 22{,}299.$$

$$2\Delta S_{[S]}(J/K) = \int_{392}^{718} 2C_P^{[S]}\,dT/T = 40.98.$$

$$\text{(d)}\ \begin{array}{c}\underbrace{2\Delta H^{\mathrm{Tr}}_{369}(J) = \quad 736}\\ \langle S\rangle\alpha \rightarrow \langle S\rangle\beta\\ \overbrace{2\Delta S^{\mathrm{Tr}}_{369}(J/K) = 1.99}\end{array} \quad \begin{array}{c}\underbrace{2\Delta H^{\mathrm{Tr}}_{392}(J) = 2{,}452}\\ \langle S\rangle\beta \rightarrow [S]\\ \overbrace{2\Delta S^{\mathrm{Tr}}_{392}(J/K) = 6.26}\end{array} \quad \begin{array}{c}\underbrace{(1)\,\Delta H^{\mathrm{Tr}}_{718}(J) = -20{,}920.}\\ S_2(g) \rightarrow [S]\\ \overbrace{(1)\,\Delta S^{\mathrm{Tr}}_{718}(J/K) = -29.14.}\end{array}$$

(e) *Calculation of* $\Delta H_{S_2(g)}$ *and* $\Delta H^\circ_{S_2(g)}$: The left-hand side of the thermodynamic loop illustrates that S_2(g) follows an *isothermal* path from State 1 to State 2 and an *isobaric* path from State 2 to State 3. $\Delta H_{S_2(g)}$ applies to the isothermal path and $\Delta H^\circ_{S_2(g)}$ applies to the isobaric path. $\Delta H_{S_2(g)} = 0$ because the isothermal enthalpy change of an ideal gas is zero regardless of the pressure path (see Appendix). Integrating the constant pressure molar heat capacity of sulfur gas, $C_P^{S_2(g)}$, from State 2 to State 3,

$$\Delta H^\circ_{S_2(g)}(J/\text{mol}) = \int_T^{718} C_P^{S_2(g)}\, dT$$

$$= 6313.9 - 8.54T - 0.14 \times 10^{-3}T^2 - 0.79 \times 10^5 T^{-1}.$$

(f) *Calculation of* $\Delta S_{S_2(g)}$ *and* $\Delta S^\circ_{S_2(g)}$: $\Delta S_{S_2(g)}$ applies to the isothermal path from State 1 to 2 and $\Delta S^\circ_{S_2(g)}$ applies to the isobaric path from State 2 to 3. The *isothermal* molar entropy change of an ideal gas (see Appendix) is $\Delta S = \int_{P_1}^{P_2} (-R/P)dP$ where R is the gas constant and P_1 and P_2 are initial and final gas pressures respectively. Hence, $\Delta S_{S_2(g)}[J/(\text{mol} \cdot \text{K})] = \int_{P_{S_2(g)}}^{1\,\text{atm}} (-R/P)dP = R\ln(P_{S_2(g)})$. Integrating the constant pressure molar heat capacity of S_2(g), $C_P^{S_2(g)}$, along the isobaric path,

$$\Delta S^\circ_{S_2(g)}[J/(\text{mol} \cdot \text{K})] = \int_T^{718} C_P^{S_2(g)}\, dT/T = 56.44 - 0.28 \times 10^{-3}T$$

$$- (0.79 \times 10^3)/2T^2 - 8.54 \times \ln(T).$$

(4) *Solve*. Equations (1), $\Sigma\Delta H_{\text{TL}} = 0$ and $\Sigma\Delta S_{\text{TL}} = 0$, from Step 2 now can be solved for ΔH_T^{Tr} and ΔS_T^{Tr} by using the enthalpy and entropy expressions derived in Step 3:

$$\Delta H_T^{\text{Tr}}(J/\text{mol}) = -55{,}900 + 21.42T + 25.98 \times 10^{-3}T^2 - 0.79 \times 10^5 T^{-1}.$$

$$\Delta S_T^{\text{Tr}}[J/(\text{mol} \cdot \text{K})] = -221.43 + 21.42 \ln(T) + 51.96 \times 10^{-3}T - 39{,}500T^{-2}$$

$$+ R \ln[P_{S_2(g)}].$$

Assuming equilibrium at $P_{S_2(g)}$ and $T(K)$, Gibbs free energy change for the transformation is:

$$\Delta G_T^{\text{Tr}} = \Delta H_T^{\text{Tr}} - T\Delta S_T^{\text{Tr}} = 0 \tag{5}$$

The $P_{S_2(g)} - T$ relationship is obtained by substituting the expressions for ΔH_T^{Tr} and ΔS_T^{Tr} into Equation (5) and solving for $\ln[P_{S_2(g)}]$:

$$\ln[P_{S_2(g)}] = 29.21 - 3.12 \times 10^{-3}T - 6{,}686T^{-1}$$

$$- 4{,}750.8T^{-2} - 2.58 \ln(T) \tag{6}$$

where T is in degrees Kelvin and $P_{S_2(g)}$ is in atm.

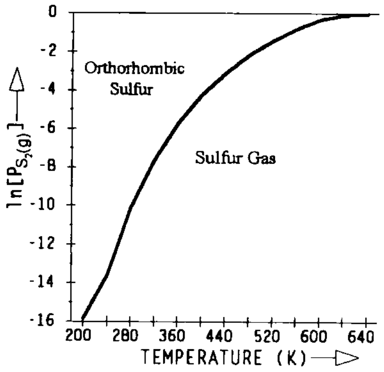


Figure 4. Stability diagram for condensation of orthorhombic sulfur from anthracite gas. Partial pressure $P_{S_2}(g) < 1$ atm. Diagram is applicable to all sulfur precipitating gas mixtures within this pressure range. Higher total gas pressure corrections are possible.

The stability diagram, constructed by graphing Equation (6), is shown in Figure 4. Stability regions are labeled in accordance with Le Châtelier's principle. The region to the left of the *equilibrium curve* is stable to orthorhombic sulfur whereas the region to the right of the curve is stable to gaseous sulfur.

Figure 4 may have utility in monitoring the release of $S_2(g)$ into the atmosphere. By monitoring $P_{S_2(g)}$, one can determine the minimum condensation temperature, T_{min}, for the formation of orthorhombic sulfur. For example, at $P_{S_2(g)} \approx 4.6 \times 10^{-2}$ atm, $T_{min} = 440$ K.

If appropriate thermodynamic data are available, TL analysis can be used to derive stability diagrams for mineral condensates of vented gases associated with any geologic process. These diagrams may prove useful in monitoring the release of noxious fumes into the atmosphere.

CONCLUSIONS

The anthracite smokers of eastern Pennsylvania are mine-related fires. Sulfur, one of the most abundant mineral condensates associated with gaseous exhalations from the smokers, may condense as an orthorhombic polymorph. Using thermodynamic loop analysis, it is possible to construct a $P_{S_2(g)} - T$ stability diagram for anthracite gas and orthorhombic sulfur. The stability diagram readily identifies partial pressure and temperature combinations that are stable to either gaseous or solid sulfur.

Thermodynamic loop analysis is a method of organization whereby the known state of a system is combined with thermodynamic properties of materials obtainable from the literature to calculate system properties in another state. TL analysis is an effective tool for unraveling the thermodynamic complexities of chemical systems because it divides a problem into parts and graphically structures it in such a manner as to provide a clearly depicted solution path.

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REFERENCES

Anthony, J. W., Williams, S. A., and Bideaux, R. A., 1977, Mineralogy of Arizona: Univ. Arizona Press, Tucson, Arizona, 255 p.

DeKok, D., 1986, Unseen danger: Univ. Pennsylvania Press, Philadelphia, 299 p.

Dunn, P. J., Peacor, D. R., Criddle, A. J., and Finkelman, R. B., 1986, Laphamite, an arsenic selenide analogue of orpiment, from burning anthracite deposits in Pennsylvania: Mineral. Magazine, v. 50, pt. 2, p. 279-282.

Finkelman, R. B., and Mrose, M. E., 1977, Downeyite, the first verified natural occurrence of SeO_2: Am. Mineralogist, v. 62, no. 3-4, p. 316-320.

Geissinger, J., 1990, Managing underground mine fires: the case of Centralia, Pennsylvania: The Pennsylvania Geographer, v. 28, no. 2, p. 22-26.

Johnson, D. L., and Stracher, G. B., 1994, Thermodynamic loop applications in materials systems (1st ed.), v. 1: The Minerals, Metals, and Materials Society of The American Institute of Mining, Metallurgical and Petroleum Engineering Inc., Warrendale, Pennsylvania, 216 p.

Jones, G. W., and Scott, G. S., 1939, Chemical considerations relating to fires in anthracite refuse: U.S. Bur. Mines Rept. of Invest. 3468, 13 p.

Lapham, D. M., Barnes, J. H., Downey, W. F., Jr., and Finkelman, R. B., 1980, Mineralogy associated with burning anthracite deposits of eastern Pennsylvania: Pennsylvania Geol. Survey Mineral Res. Rept. 78, 82 p.

Limacher, D., 1963, A propos de la formation de minéraux secondaires lors de la combustion des charbons: Societe Geologique du Nord, Annales, 83, p. 287-288.

Stoiber, R. E., and Rose, W. I., Jr., 1974, Fumarole incrustations at active Central American volcanoes: Geochimica et Cosmochimica Acta, v. 38, no. 4, p. 495-516.

Stracher, G. B., 1993, Thermodynamically calculated P-T curve for the condensation of crystalline sulfur from anthracite coal gas: eastern Pennsylvania: Geol. Soc. America, Abstracts with Programs, v. 25, p. A-193.

Stracher, G. B., and Johnson, D. L., 1989, Thermodynamic Loops: theoretical applications to solid-solid mineral transformations and phase equilibria: The Compass, v. 66, no. 4, p. 185-188.

Weast, R. C., Lide, D. R., Astle, M. J., and Beyer, W. H., eds., 1989, Handbook of chemistry and physics (70th ed.): CRC Press, Inc., Boca Raton, Florida, 2 volumes.

Wood, G. H., Jr., and Bergin, M. J., 1970, Structural controls of the Anthracite region, Pennsylvania, *in* Fisher, G. W., Pettijohn, F. J., Reed, Jr., J. C., and Weaver, K. N., eds., Studies of Appalachian geology: central and southern: John Wiley & Sons, Inc., New York, p. 147-160.

APPENDIX: THERMODYNAMIC PROOFS

A.1. Isothermal Enthalpy Change of an Ideal Gas

Method 1. The enthalpy, H, of a substance is defined by $H = U + PV$ where U, P, and V designate internal energy, pressure, and volume respectively. Applying the chain rule,

$$dH = dU + d(PV) \tag{7}$$

For an ideal gas, $U = f(T)$ only (Johnson and Stracher, 1994). Hence, $dU = 0$ at constant temperature. Because $PV = RT$ for an ideal gas, $d(PV) = d(RT) = RdT + TdR = 0$. Substituting into (7),

$$\int_{H_1}^{H_2} dH = \Delta H = 0$$

Method 2. Applying the chain rule to the enthalpy function $H = f(T, P)$,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \cancelto{0}{\left(\frac{\partial H}{\partial T}\right)_P dT} \tag{8}$$

Substituting the Maxwell equation $dH = TdS + VdP$, $(\partial H/\partial P)_T\, dP = TdS + VdP$. Dividing by dP and holding T constant,

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \tag{9}$$

From the condition for an exact differential and the Maxwell equation $dG = VdP - SdT$ (Johnson and Stracher 1994),

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{10}$$

Substituting (10) into (9),

$$\left(\frac{\partial H}{\partial P}\right)_T = \cancelto{0}{-T\left(\frac{\partial V}{\partial T}\right)_P + V} \tag{11}$$

From the ideal gas equation $PV = RT$ where V is molar volume, $(\partial V/\partial T)_P = R/P$. Substituting into (11), $(\partial H/\partial P)_T = -TR/P + V = 0$. Hence,

$$\int_{H_1}^{H_2} dH = \Delta H = 0$$

A.2. Isothermal Entropy Change of an Ideal Gas

Applying the chain rule to the entropy function $S = f(P, T)$,

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \cancelto{0}{\left(\frac{\partial S}{\partial T}\right)_P dT}$$

Substituting (10), $dS = -(\partial V/\partial T)_P\, dP$. For an ideal gas, $V = RT/P$ and therefore

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\frac{RT}{P}\right)_P = R/P.$$

Hence,

$$dS = -RdP/P \Rightarrow \int_{S_1}^{S_2} dS = \int_{P_1}^{P_2} -RdP/P$$

or

$$\Delta S = \int_{P_1}^{P_2} (-R/P)\, dP$$