Since H does not have an absolute value (only changes in H can be measured), it is convenient to introduce a convention which will allow the comparison of different enthalpy–temperature diagrams. This convention assigns the value of zero to the enthalpy of *elements in their stable states at 298 K* (25°C) and $P = 1$ atm. Thus, the enthalpy of a compound at 298 K and $P = 1$ atm is simply the enthalpy of formation

of one mole of the compound from its elements at 298 K and $P = 1$ atm. For example, for the oxidation reaction

$$M_{(\mathrm{solid})} + \frac{1}{2}O_{2(\mathrm{gas})} = MO_{(\mathrm{solid})} \text{ at 298 K and } P = 1 \text{ atm}$$

$$\Delta H_{298} = H_{\mathrm{MO}(s)298} - H_{\mathrm{M}(s)298} - \frac{1}{2}H_{\mathrm{O}_2(g)298}$$

and, since $H_{\mathrm{M},298}$ and $H_{\mathrm{O}_2,298}$ are by convention set equal to zero, then

$$\Delta H_{298} = H_{\mathrm{MO},298}$$

- تغییرات انتالپی (حرارت واکنش) با دما در فشار ثابت در نمودار انتالپی- دما نشان داده شده است

$$Pb + \frac{1}{2}O_2 = PbO$$

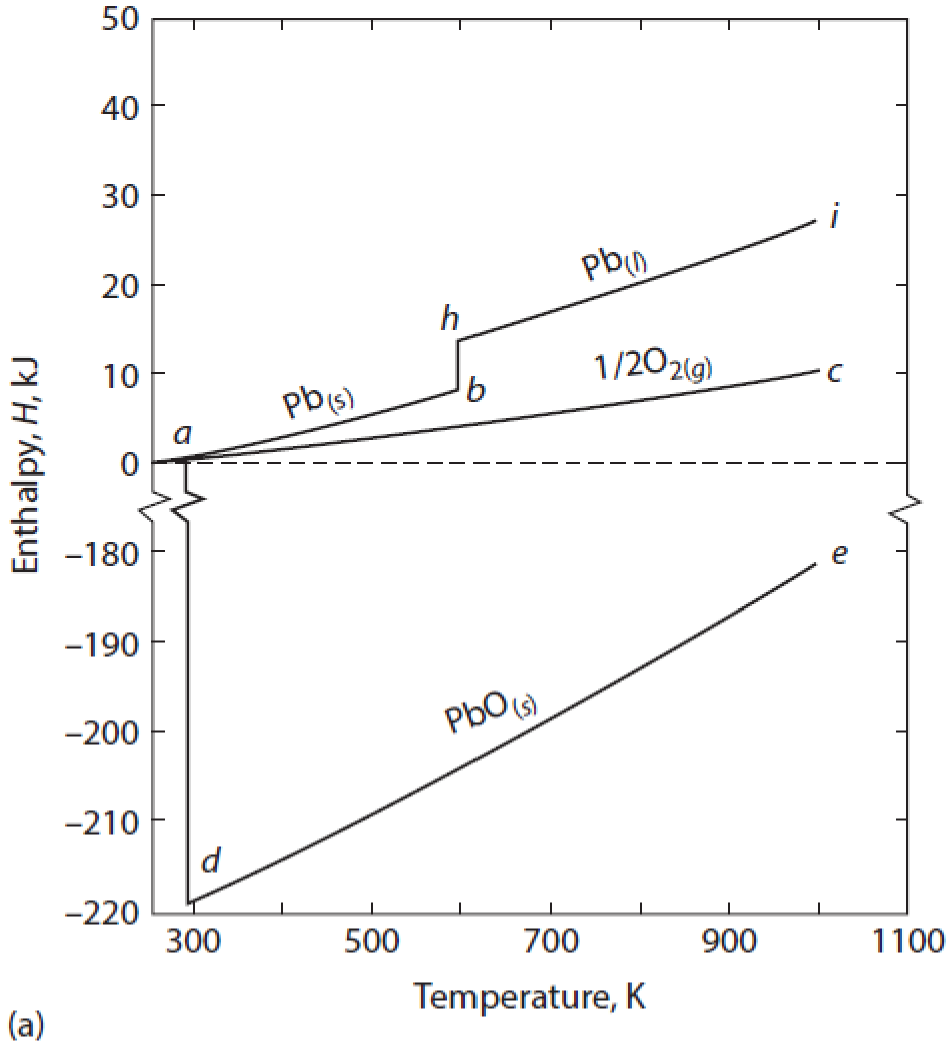


Figure 6.7a (a) The variation, with temperature, of the enthalpies of $Pb_{(s)}$, $Pb_{(l)}$, $1/2O_{2(g)}$, and $PbO_{(s)}$.

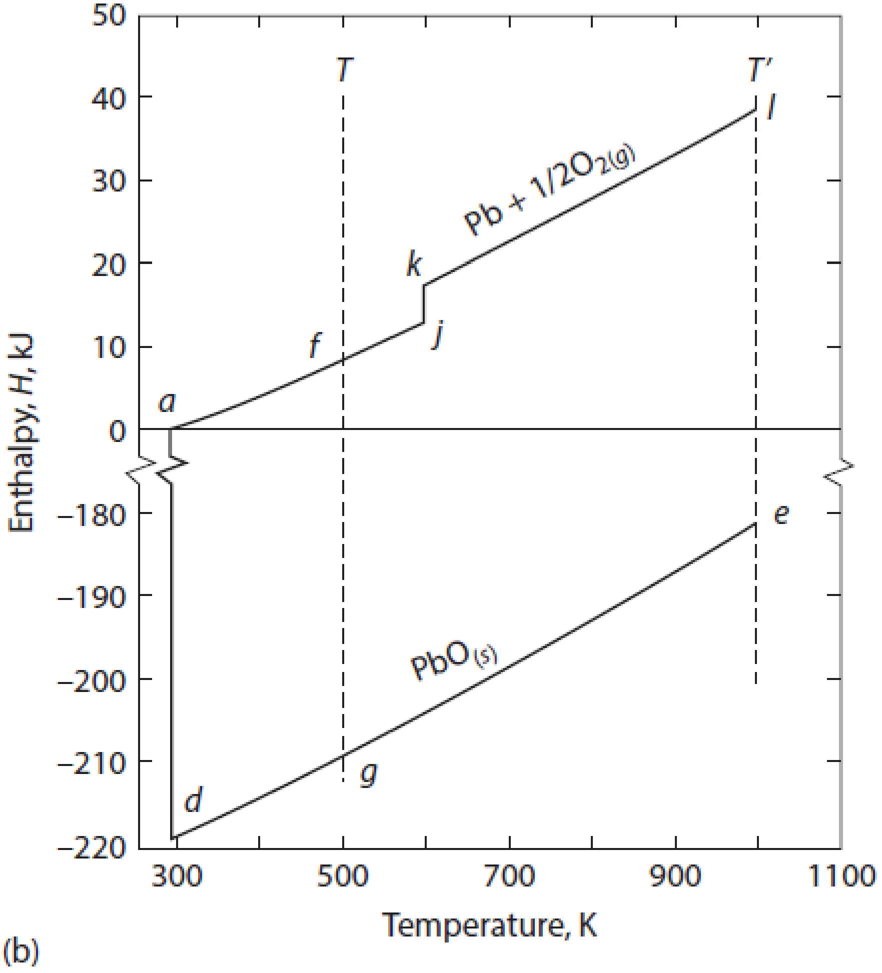


Figure 6.7b (b) The variation, with temperature, of the enthalpies of (Pb + 1/2O_2) and PbO.

Table 6.1 Thermochemical Data for Pb, PbO, and O_2

$H_{\mathrm{Pbo}(298)} = -219{,}000$ J/K

$c_{p,\mathrm{Pb}(s)} = 23.6 + 9.75 \times 10^{-3}T$ J/K from 298 K to $T_{\mathrm{m,Pb}}$

$c_{p,\mathrm{Pb}(l)} = 32.4 - 3.1 \times 10^{-3}T$ J/K from $T_{\mathrm{m,Pb}}$ to 1200 K

$c_{p,\mathrm{PbO}(s)} = 37.9 + 26.8 \times 10^{-3}T$ J/K from 298 K to $T_{\mathrm{m,Pbo}}$

$c_{p,\mathrm{O_2}(g)} = 29.96 + 4.18 \times 10^{-3}T - 1.67 \times 10^{5}T^{-2}$ J/K from 298 K to 3000 K

$\Delta H_{\mathrm{m,Pb}} = 4810$ J at $T_{\mathrm{m,Pb}} = 600$ K

$T_{\mathrm{m,PbO}} = 1159$ K

In Figure 6.7a:

- *a* represents the enthalpy of 1/2 mole of oxygen gas and 1 mole of $\mathrm{Pb}_{(s)}$ at 298 K (set = 0 by convention).
- *ab* represents the variation of $H_{\mathrm{Pb}(s)}$ with temperature in the range $298 \leq T \leq 600$ K, where $H_{\mathrm{Pb}(s)}, T$ is given by $\int_{298}^{T} c_{p,\,\mathrm{Pb}(s)}\, dT$.
- *ac* represents the variation of $H_{\frac{1}{2}\mathrm{O}_2(g)}$ with temperature in the range $298 < T < 3000$ K, where $H_{\frac{1}{2}\mathrm{O}_2(g)}$ is given by $\frac{1}{2}\int_{298}^{T} c_{p,\mathrm{O}_2(g)}\, dT$.
- *ad* is $\Delta H_{\mathrm{PbO}(s),298\ \mathrm{K}} = -219{,}000$ J.
- *de* represents the variation of $H_{\mathrm{PbO}(s)}$ with temperature in the range 298 K $\leq T \leq$ 1159 K, where $H_{\mathrm{PbO}(s),T} = -219{,}000 + \int_{298}^{T} c_{p,\mathrm{PbO}(s)} dT$ J.

In Figure 6.7b:

- *a* represents the enthalpy of 1/2 mole of $O_{2(g)}$ and 1 mole of $Pb_{(s)}$ at 298 K.
- *f* represents the enthalpy of 1/2 mole of $O_{2(g)}$ and 1 mole of $Pb_{(s)}$ at the temperature *T*.
- *g* represents the enthalpy of 1 mole of $PbO_{(s)}$ at the temperature *T*.

$$\begin{aligned}\Delta H_{\text{PbO},298\text{ K}} &= \Delta H(a \rightarrow f) + \Delta H(f \rightarrow g) + \Delta H\ (g \rightarrow d) \\ &= \int_{298}^{T} \left(\frac{1}{2} c_{p,\text{O}_2(g)} + c_{p,\text{Pb}(s)} \right) dT + \Delta H_{\text{PbO},T} + \int_{T}^{298} c_{p,\text{PbO}(s)} dT\end{aligned}$$

and thus,

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta c_p dT$$

where:

$$\Delta c_p = c_{p,\text{PbO}(s)} - c_{p,\text{Pb}(s)} - \frac{1}{2} c_{p,\text{O}_2(g)}$$

From the data in Table 6.1,

$$\Delta c_p = -0.7 + 14.96 \times 10^{-3} T + 0.85 \times 10^{5} T^{-2}$$

range of temperature from 298 to 600 K ($T_{m,\mathrm{Pb}}$):

$$\begin{aligned}\Delta H_T \quad &= -219{,}000 + \int_{298}^{T} (-0.7 + 14.96\times10^{-3}T + 0.85\times10^{5}T^{-2})dT \\ &= -219{,}000 - 0.7(T-298) + 7.48\times10^{-3}(T^2 - 298^2) \\ &\quad - 0.85\times10^{5}\left(\frac{1}{T} - \frac{1}{298}\right)\end{aligned}$$

$T = 500$ K, this gives $\Delta H_{500\ \mathrm{K}} = -217{,}800$ J,

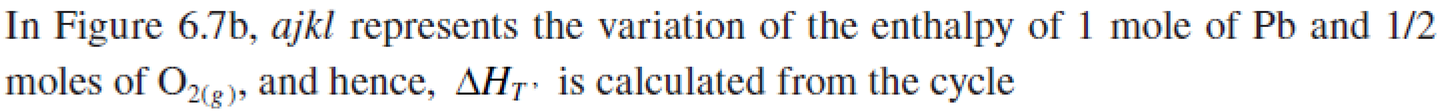
- اگر واکنش در دمایی انجام شود که یک یا چند محصول دچار تغییر فاز شوند باید تغییرات انتالپی این فرایندها در نظر گرفته شود به عنوان مثال در دمای ۶۰۰ درجه سانتی گراد ذوب Pb صورت می گیرد

$$H_{\mathrm{Pb}(l),600\mathrm{K}} = \int_{298}^{600} c_{p,\mathrm{Pb}(s)} dT + \Delta H_{m,\mathrm{Pb}}$$

- و اگر دما بالاتر از 600K باشد

$$H_{\mathrm{Pb}(l),T} = \int_{298}^{600} c_{p,\mathrm{Pb}(s)} dT + \Delta H_{m,\mathrm{Pb}} + \int_{600}^{T} c_{p,\mathrm{Pb}(l)} dT$$

- در شکل 6-7b خط ajkl تغییرات انتالپی یک مول Pb و ۱/۲ مول O2 را نشان می دهد و از سیکل به صورت زیر محاسبه می شود



In Figure 6.7b, *ajkl* represents the variation of the enthalpy of 1 mole of Pb and 1/2 moles of $O_{2(g)}$, and hence, $\Delta H_{T'}$ is calculated from the cycle

$$\Delta H_{298\,\mathrm{K}} = \Delta H(a \to d) = \Delta H(a \to j) + \Delta H(j \to k) + \Delta H(k \to l)$$

$$+ \Delta H(l \to e) + \Delta H(e \to g) + \Delta H(g \to d)$$

where:

$$\Delta H(a \to j) = \int_{298}^{T_{m,\mathrm{Pb}}} \left(c_{p,\mathrm{Pb}(s)} + \frac{1}{2} c_{p\mathrm{O}_2(g)} \right) dT$$

$\Delta H(j \to k) =$ the latent heat of melting of Pb at $T_{m,\mathrm{Pb}} = 4810$ J

$$\Delta H(k \to l) = \int_{T_{m,Pb}}^{T} \left(c_{p,\mathrm{Pb}(l)} + \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$

$$\Delta H(l \to e) = \Delta H_T$$

$$\Delta H(e \to g) = \int_{T}^{T_{m,\mathrm{Pb}}} c_{p,\mathrm{PbO}(s)} dT$$

$$\Delta H(g \to d) = \int_{T_{m,\mathrm{Pb}}}^{298} c_{p,\mathrm{PbO}(s)} dT$$

Thus,

$$\Delta H_T = \Delta H_{298K} + \int_{298}^{T_{m,\mathrm{Pb}}} \left(c_{p,\mathrm{PbO}(s)} - c_{p,\mathrm{Pb}(s)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$

$$- \Delta H_{m,\mathrm{Pb}} + \int_{T_{m,\mathrm{Pb}}}^{T} \left(c_{p,\mathrm{PbO}(s)} - c_{p,\mathrm{Pb}(l)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$

$$= -219{,}000 + \int_{298}^{600} (-0.7 + 14.96 \times 10^{-3} T + 0.85 \times 10^{5} T^{-2}) dT$$

$$- 4810 + \int_{600}^{T} (-9.3 + 27.8 \times 10^{-3} T + 0.85 \times 10^{5} T^{-2}) dT$$

$\Delta H_{1000} = -216{,}700$ J at $T' = 1000$ K,

- در حالت کلی برای واکنش زیر

$$\mathrm{M} + \frac{1}{2}\mathrm{O}_2 = \mathrm{MO}$$

$$\begin{aligned}
\Delta H_T = \Delta H_{298} &+ \int_{298}^{T_{m,\mathrm{M}}} \left(c_{p,\mathrm{MO}(s)} - c_{p,\mathrm{M}(s)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT \\
- \Delta H_{m,\mathrm{M}} &+ \int_{T_{m,\mathrm{M}}}^{T_{m,\mathrm{MO}}} \left(c_{p,\mathrm{MO}(s)} - c_{p,\mathrm{M}(l)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT \\
+ \Delta H_{m,\mathrm{MO}} &+ \int_{T_{m,\mathrm{MO}}}^{T} \left(c_{p,\mathrm{MO}(l)} - c_{p,\mathrm{M}(l)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT
\end{aligned}$$

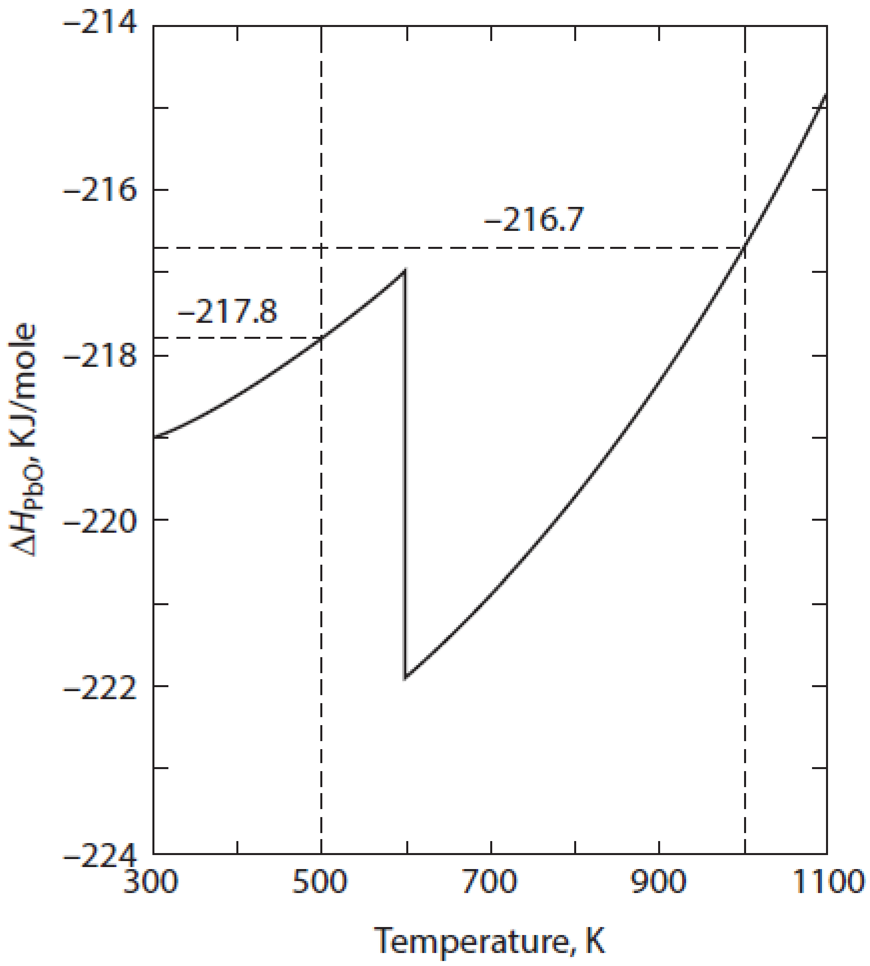


Figure 6.8 The variation, with temperature, of the enthalpy change for the reaction Pb + $1/2O_2$ = PbO.

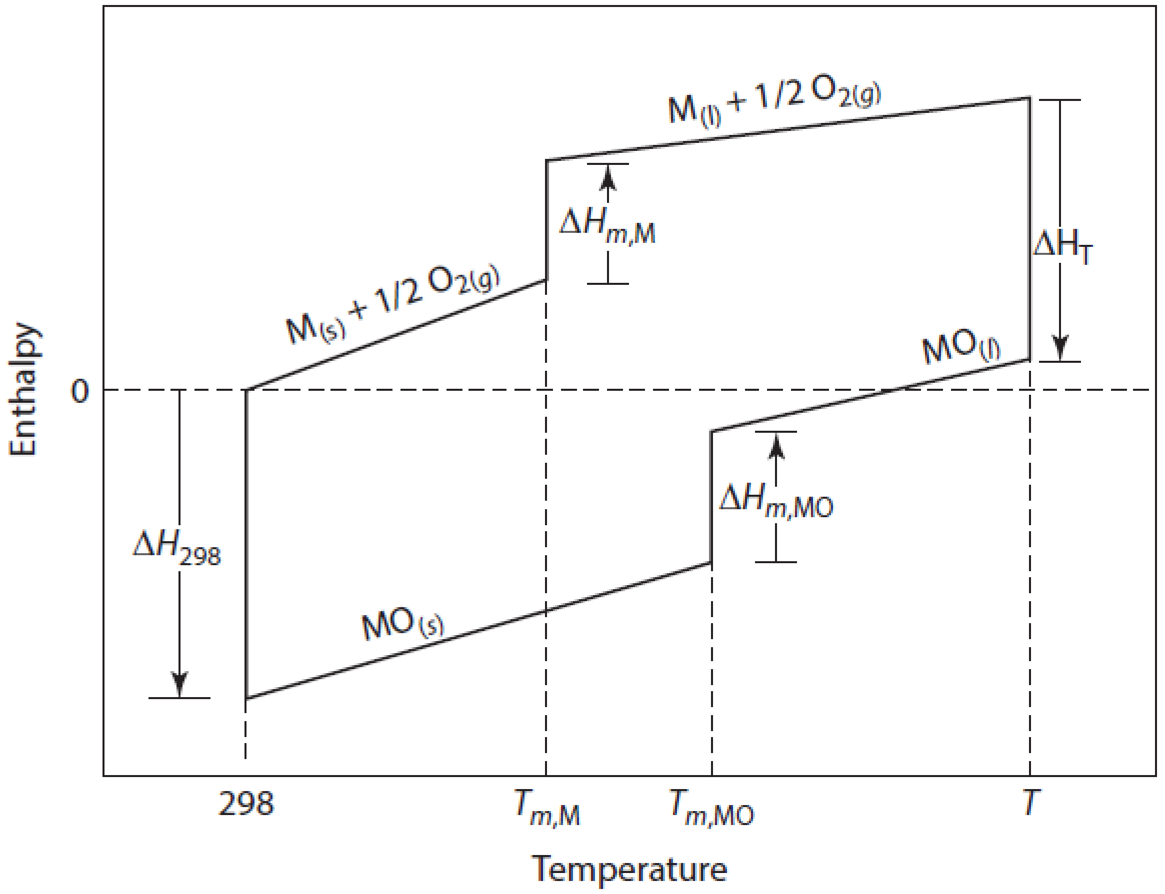


Figure 6.9 The effect of phase changes on ΔH for a chemical reaction.

- مطابق اصل لوشاتلیه : اگر تغییری در سیستم در حال تعادل باشد اگر تغییری از خارج به سیستم اعمال شود انگاه سیستم به سمتی می رود که این تغییر را خنثی کند

- بنابراین در مورد انتالپی واکنش ها برای تعیین علامت تغییرات انتالپی: اگر فاز دمای پایین در تعادل با فاز دمای بالا باشد انگاه اگر به سیستم حرارت وارد شود سیستم به سمتی می رود که این اثر حرارتی را خنثی کند یعنی فرایند گرماگیر در سیستم رخ می دهد

Kirchhoff’s law

- اگر در فاریندی تغییرات فازی الفا به بتا صورت گیرد وفاز دمای بالا فاز بتا باشد آنگاه

$$\text{For } \alpha\text{:} \quad \left(\frac{\partial H_\alpha}{\partial T}\right)_P = c_p^\alpha$$

$$\text{For } \beta\text{:} \quad \left(\frac{\partial H_\beta}{\partial T}\right)_P = c_p^\beta$$

Subtraction gives

$$\left(\frac{\partial H_\beta}{\partial T}\right)_P - \left(\frac{\partial H_\alpha}{\partial T}\right)_P = c_p^\beta - c_p^\alpha$$

$$\left(\frac{\partial (H_\beta - H_\alpha)}{\partial T}\right)_P = \Delta c_p$$

or

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta c_p \tag{6.10}$$

and integrating from state 1 to state 2 gives

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta c_p dT \tag{6.11}$$

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H(T_2) - \Delta H(T_1) = \int_{T_1}^{T_2} \Delta c_p dT$$

closed system reversible process

$$dS = \frac{\delta q_{\text{rev}}}{T} \qquad (3.8)$$

$$dS = \left(\frac{\delta q_{\text{rev}}}{T}\right)_P = \left(\frac{dH}{T}\right)_P = \frac{c_p dT}{T}$$

$$\Delta S = S(T_2, P) - S(T_1, P) = \int_{T_1}^{T_2} \frac{c_p}{T} dT \tag{6.12}$$

area under a plot of c_p/T versus T

$$S_T = S_0 + \int_0^T \frac{c_p}{T} dT \tag{6.13}$$

S_0 is the molar entropy of the system at 0 K.

$$\Delta G = \int_0^T c_P dT - T\int_0^T \frac{c_p}{T} dT - TS_0$$

Le Chatelier in 1888:

- اگر مقدار S_0 مشخص باشد می توان مقادیر تغییرات انرژی آزاد گیبس را محاسبه نمود

1902, Richards (Theodore William Richards, 1868–1928)

for many reactions,

$$\text{as } T \to 0 \quad \left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P = 0$$

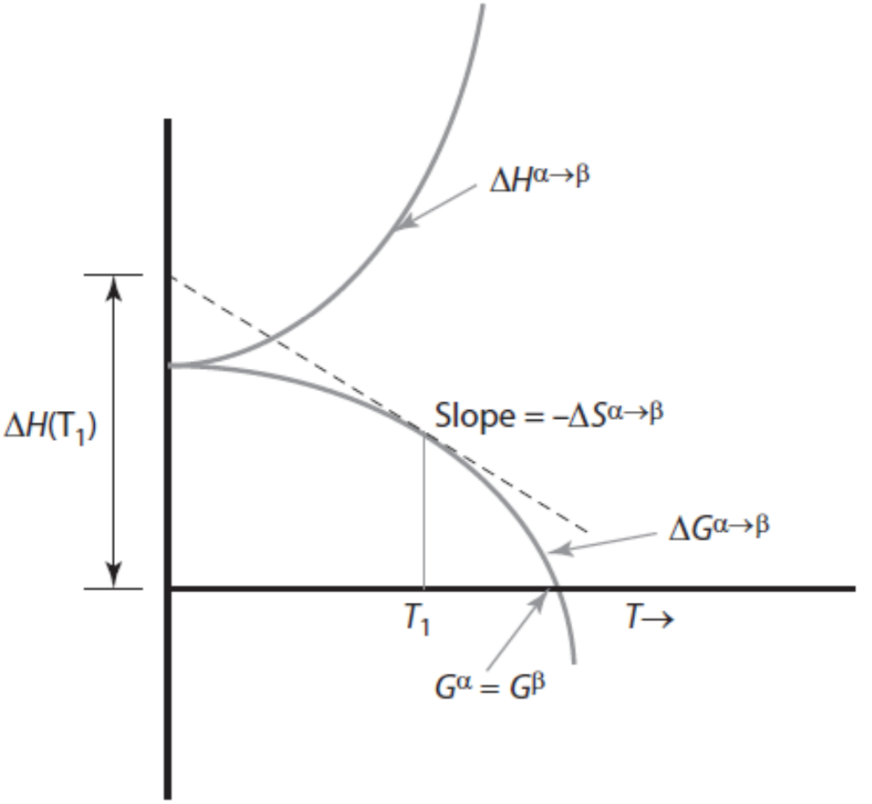
1906, Nernst (Walther Hermann Nernst 1864–1941)

Nernst heat theorem.

- نرنست فرض کرد این موضع برای همه مواد صادق باشد

chemical reaction at the constant temperature T)

$$\Delta G_T = \Delta H_T - T\Delta S_T$$



.10 The variation of the change in the Gibbs free energy and the enthalpy for a reaction with temperature. As the temperature approaches absolute zero, thei values approach each other and their slopes approach 0.

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P - T\left(\frac{\partial \Delta S}{\partial T}\right)_P - \Delta S$$

But,

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

and thus,

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = T\left(\frac{\partial \Delta S}{\partial T}\right)_P = \Delta c_p$$

$\left(\partial \Delta G/\partial T\right)_p$ and $\left(\partial \Delta H/\partial T\right)_p$ approach zero as $T \to 0$,

ΔS and Δc_p approach zero as $T \to 0$

- بنابراین

$$A + B = AB$$

$$\Delta S = S_{AB} - S_A - S_B = 0 \text{ at } T = 0,$$

Planck (Max Karl Ernst Ludwig Planck, 1858–194

entropy of any homogeneous substance

which is in complete internal equilibrium is zero at 0 K.

Nernst–Planck–Simon statement (Francis Simon, 1893–1956) of the Third Law.

6.5.2 Apparent Contradictions to the Third Law of Thermodynamics

1. Glasses are noncrystalline solids
2. Solutions are mixtures of atoms, ions, or molecules,
3. mixtures of isotopes,
4. vacant lattice sites,
5. Random crystallographic orientation of molecules in the crystalline state

6.6 EXPERIMENTAL VERIFICATION OF THE THIRD LAW

$$\alpha \to \beta$$

$$\Delta S_{\mathrm{IV}} = \Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} + \Delta S_{\mathrm{III}}$$

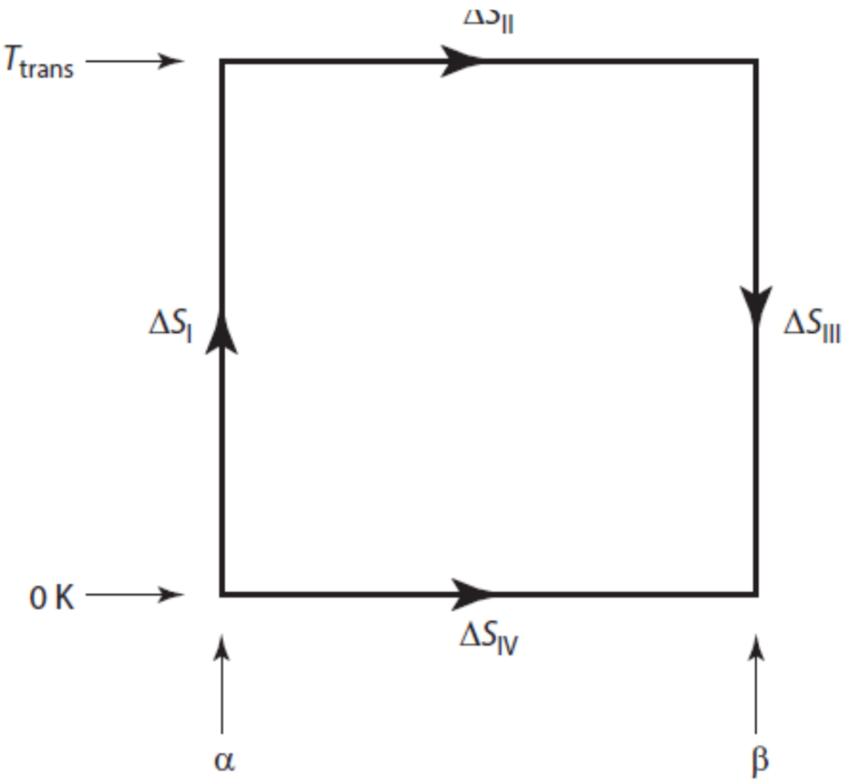
$$\Delta S_{\mathrm{IV}} = 0$$

$$\Delta S_{\mathrm{II}} = -(\Delta S_{\mathrm{I}} + \Delta S_{\mathrm{III}})$$

$$\Delta S_{\mathrm{I}} = \int_{0}^{T_{\mathrm{trans}}} \frac{c_{p(\alpha)}}{T} dT$$

$$\Delta S_{\mathrm{II}} = \frac{\Delta H_{\mathrm{trans}}}{T_{\mathrm{trans}}} = H(\beta, T_{\mathrm{trans}}) - H(\alpha, T_{\mathrm{trans}}$$

$$\Delta S_{\mathrm{III}} = \int_{T_{\mathrm{trans}}}^{0} \frac{c_{p(\beta)}}{T} dT$$



sulfur,

$$\Delta S_{\mathrm{I}} = \int_{0}^{368.5} \frac{c_{p(\mathrm{rhombic})}}{T} dT = 36.86 \text{ J/K}$$

$$\Delta S_{\mathrm{II}} = \frac{\Delta H_{\mathrm{trans}}}{T_{\mathrm{trans}}} = \frac{400}{368.5} = 1.09 \text{ J/K}$$

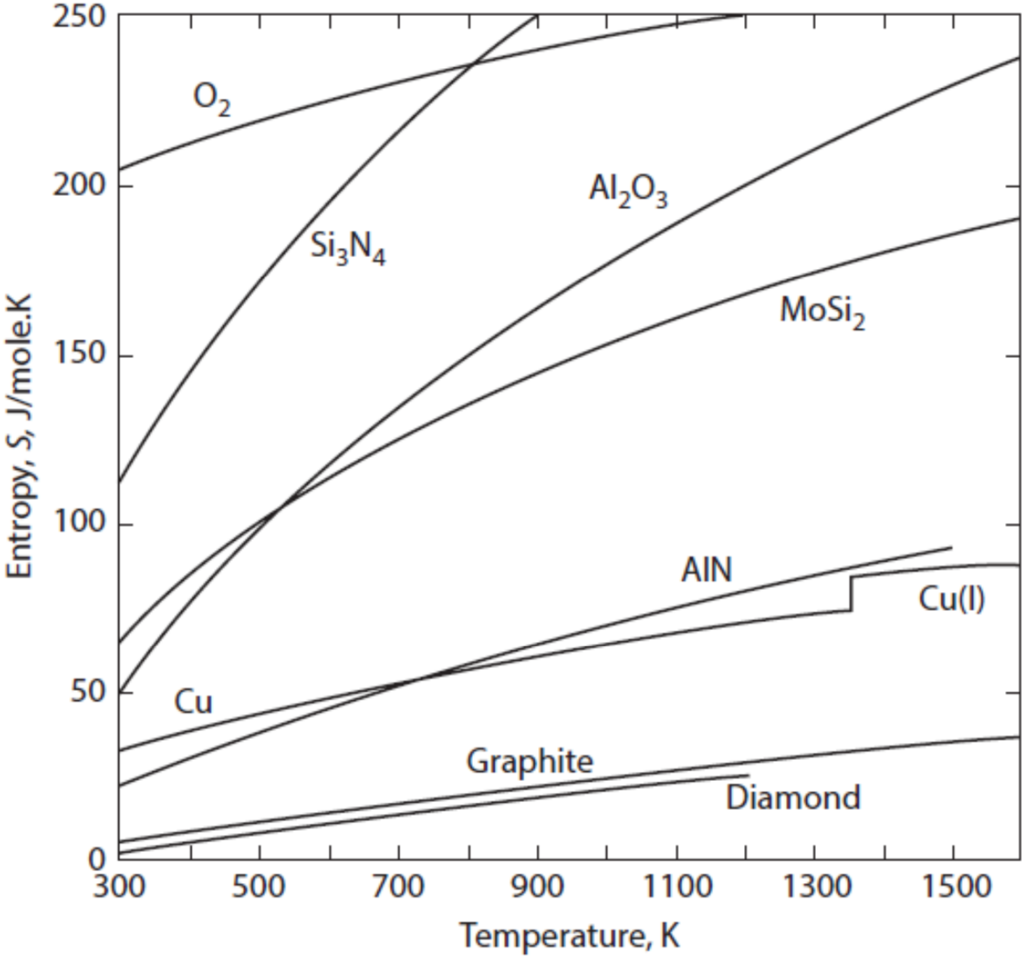
$$\Delta S_{\mathrm{III}} \int_{368.5}^{0} \frac{c_{p(\mathrm{monoclinic})}}{T} dT = -37.8 \text{ J/K}$$

$$\left(\Delta S_{\mathrm{I}} + \Delta S_{\mathrm{III}}\right) = -\left(36.86 - 37.8\right) = 0.94 \text{ J/K}$$

absolute value of the entropy

$$S_T = \int_0^T \frac{c_p}{T}\,dT \text{ J/K}$$

$$c_{p(s)} = a + bT + cT^{-2}$$

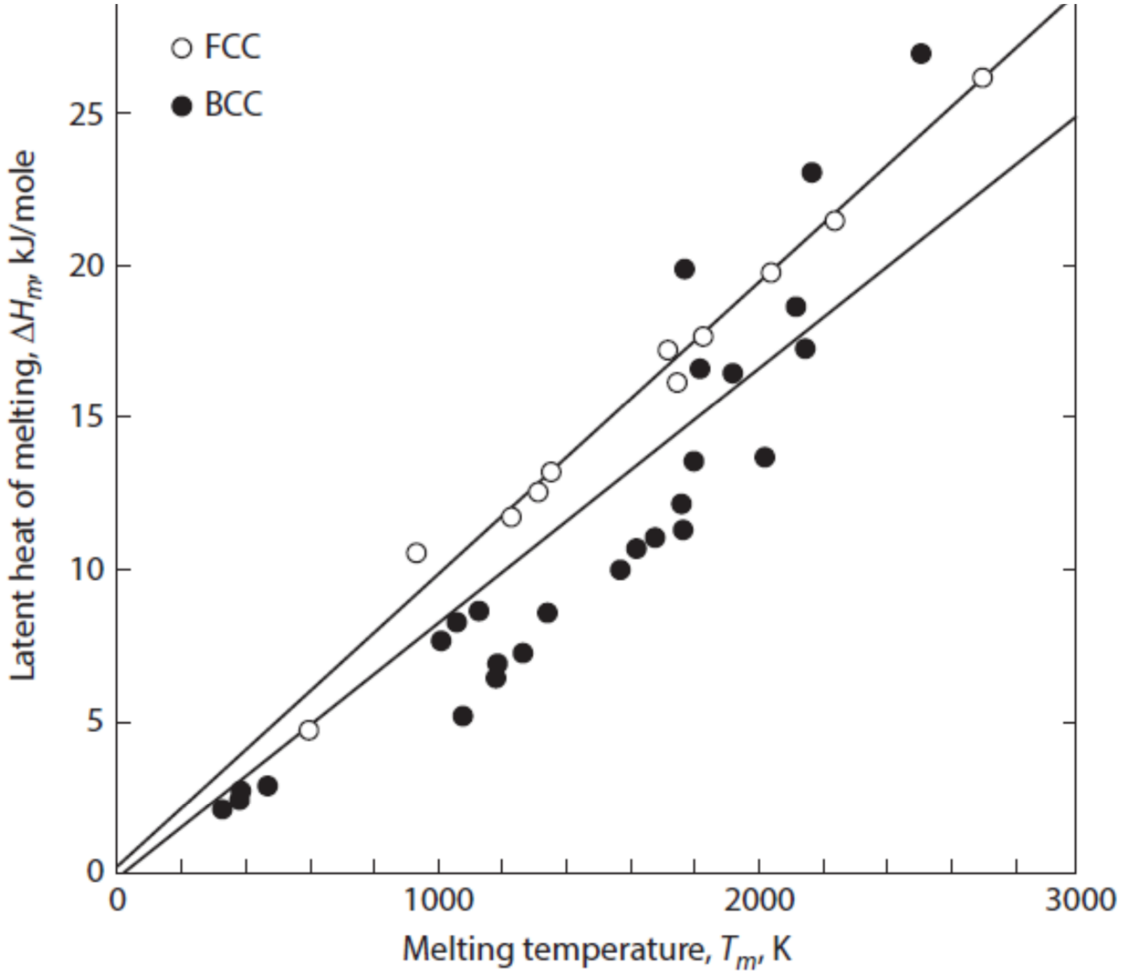


$$S_T = S_{298} + a\ln\left(\frac{T}{298}\right) + b(T-298) - \frac{1}{2}c\left(\frac{1}{T^2} - \frac{1}{298^2}\right)$$

$$S_T = S_{298} + \int_{298}^{T_m} \frac{c_{p(s)}}{T}\,dT + \Delta S_m + \int_{T_m}^{T} \frac{c_{p(l)}}{T}\,dT$$

Richards 1897

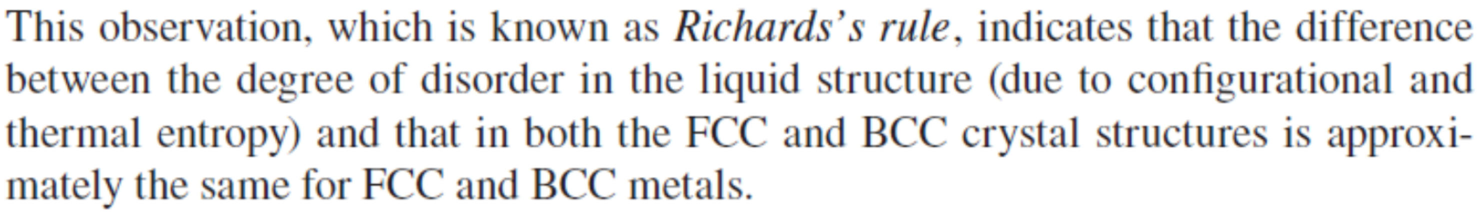
- انتروپی ذوب فلزات مقدار یکسانی دارد یا رسم انتالپی ذوب بر حسب دمای ذوب خط راست است



$$\Delta S_m^{\mathrm{FCC}} = \frac{\Delta H_m^{\mathrm{FCC}}}{T_m} = 9.6\ \mathrm{J/K}$$

$$\Delta S_m^{\mathrm{BCC}} = \frac{\Delta H_m^{\mathrm{BCC}}}{T_m} = 8.25\ \mathrm{J/K}$$

- تفاوت بین درجه بی نظمی حالت مایع (حرارتی و آرایشی) در ساختارهای BCC و FCC تقریبا یکسان است



This observation, which is known as *Richards's rule*, indicates that the difference between the degree of disorder in the liquid structure (due to configurational and thermal entropy) and that in both the FCC and BCC crystal structures is approximately the same for FCC and BCC metals.

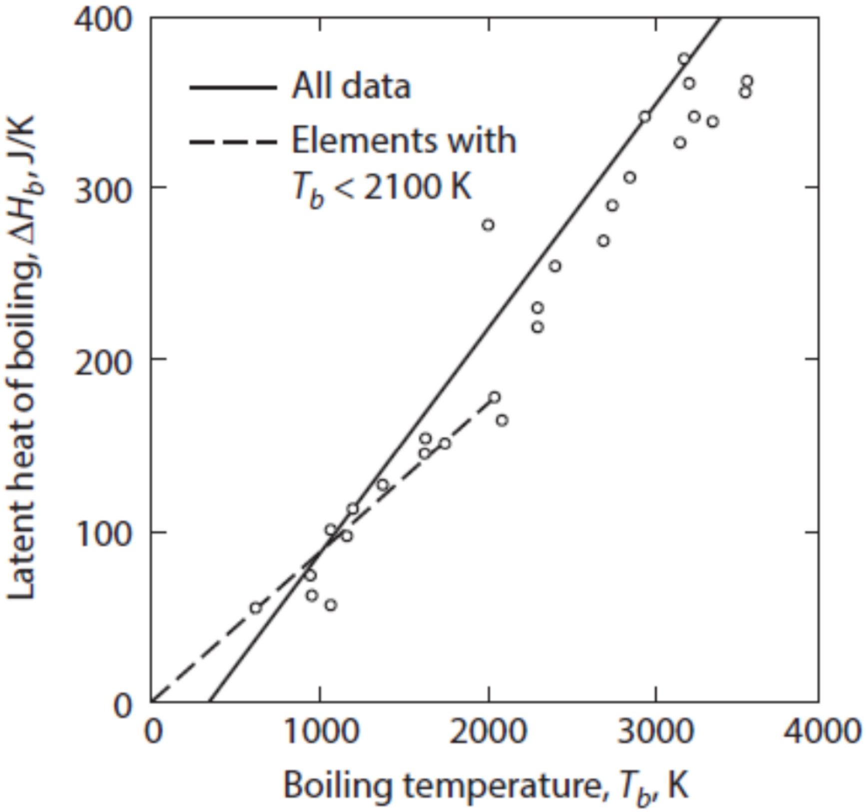
Trouton’s law (1836-1922)

- انتروپی جوش فلز مایع 88J/Kاست برای فلزات با دمای ذوب کمتر از 4000K

$$\Delta H_b = 121 T_B - 43 \text{ J/K}$$

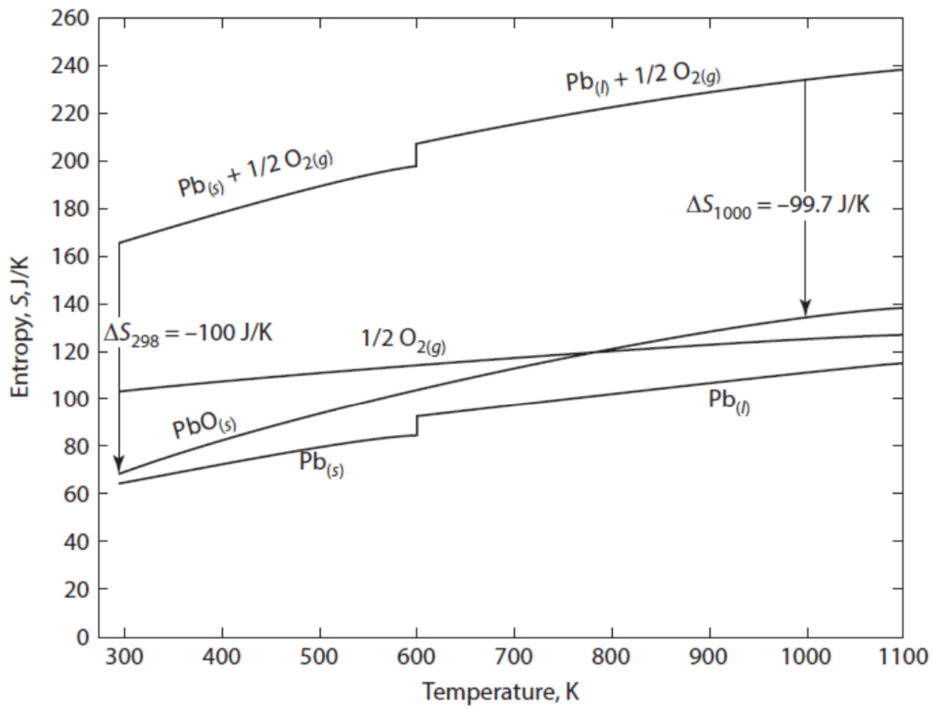
- فیت داده ها برای ۱۳ فلز با دمای ذوب کمتر از 2100 K

$$\Delta H_b = 87T_b - 0.4 \text{ J/K}$$



re 6.14 An illustration of Trouton's rule.

- انتروپی مولار جوش تقریبا 88 J/K است برای فلزات



$$Pb + \frac{1}{2}O_2 = PbO$$

igure 6.15 The variation, with temperature, of the entropies of $Pb_{(s)}$, $Pb_{(l)}$, $PbO_{(s)}$, and $1/2O_{2(g)}$, and the entropy change for the reaction $Pb + 1/2O_2 = PbO$.

$$\Delta S_T = S_{T,\mathrm{PbO}} - S_{T,\mathrm{Pb}} - \frac{1}{2}S_{T,\mathrm{O}_2} \quad \text{very nearly equal to } -1/2\, S_{T,\mathrm{O}_2}$$

6.7 THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$dH = TdS + VdP$$

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

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

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

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\alpha V + V = V(1-\alpha T)$$

$$\Delta H = H(P_2,T) - H(P_1,T) = \int_{P_1}^{P_2} V(1-\alpha T)\,dP \qquad (6.14)$$

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP$$

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

$$\left(\frac{\partial S}{\partial P} \right)_T = -\alpha V$$

$$\Delta S = S(P_2, T) - S(P_1, T) = -\int_{P_1}^{P_2} \alpha \, V dP$$

ideal gas, since $\alpha = 1/T$.

$$\Delta S = -\int_{P_1}^{P_2} R d \ln P = -R \ln\left(\frac{P_2}{P_1}\right) = R \ln\left(\frac{V_2}{V_1}\right)$$