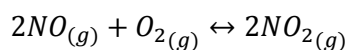


Auxiliar nº8

P1

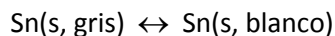
Para la siguiente transformación química el valor de $K_p = 2.3 \times 10^{12}$ a la temperatura $T = 298 \text{ K}$



Si inicialmente hay 2 moles de $NO(g)$ y 1 mol de $O_2(g)$, ¿qué grado de avance optimiza la energía libre total del sistema? Considere los gases como ideales y explique claramente las aproximaciones que haga.

P2

Considere el siguiente equilibrio entre las dos formas alotrópicas del estaño sólido

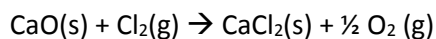


A partir de los datos de la tabla y sabiendo que ambas fases se encuentran en equilibrio a 1.0 bar y 18 °C. Calcule a que temperatura se encontrarán en equilibrio a la presión de 300 bar.

	Sn(gris)	Sn(blanco)
$S^\circ \text{ (J/ K mol)}$	42.4	51.2
$\rho \text{ (Kg/m}^3\text{)}$	5750	7280

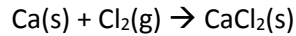
P3

Suponga que se desea preparar cloruro de calcio a partir de óxido de calcio haciendo pasar una corriente de cloro sobre una muestra de óxido de calcio



En este experimento la presión de cloro $P(Cl_2)=0,8 \text{ [atm]}$; $P(O_2)=0,2 \text{ [atm]}$ y $T= 85^\circ\text{C}$ ¿Resultará?

La reacción de formación de cloruro de calcio es:



Datos ($T = 298^\circ\text{K}$)

$$\Delta G_f^0(\text{CaO}) = -603.30 \left[\frac{\text{KJ}}{\text{mol}} \right]$$

$$C_p(\text{CaO}) = 42.8 \left[\frac{\text{J}}{^\circ\text{Kmol}} \right]$$

$$S^0(\text{CaCl}_2) = 104.62 \left[\frac{\text{J}}{^\circ\text{Kmol}} \right]$$

$$S^0(\text{Cl}_2) = 223.081 \left[\frac{\text{J}}{^\circ\text{Kmol}} \right]$$

$$\Delta H_f^0(\text{CaO}(s)) = -634.93 \left[\frac{\text{KJ}}{\text{mol}} \right]$$

$$\Delta H_f^0(\text{CaCl}_2(s)) = -785.8 \left[\frac{\text{KJ}}{\text{mol}} \right]$$

$$S^0(\text{Ca}) = 41.6 \left[\frac{\text{J}}{^\circ\text{Kmol}} \right]$$

P4

Las ecuaciones de las líneas de equilibrio de sublimación y vaporización de una cierta sustancia de $\text{PM}=400$ [gr/mol] son:

$$(1) \text{Log}P_s[\text{mmHg}] = 10,5 - 2500/T$$

$$(2) \text{Log}P_v[\text{mmHg}] = 7,5 - 1500/T$$

Y la ecuación de la curva de fusión está dada por:

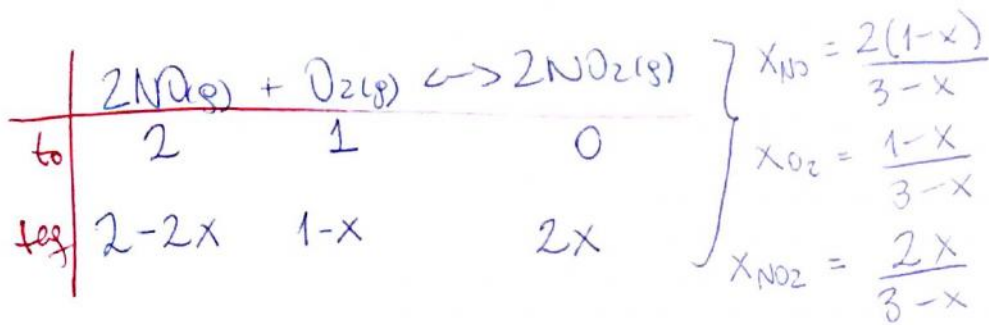
$$(3) P_f[\text{atm}] = 238,4 - 40,816 \cdot \ln(T[\text{K}])$$

Sabiendo que:

$$C_p(\text{líquido}) = 0,085 \text{ [cal/gr}^\circ\text{K}], C_p(\text{sólido}) = 0,08 \text{ [cal/gr}^\circ\text{K}], C_p(\text{gas}) = 7,0 \text{ [cal/mol}^\circ\text{K]}$$

Calcular la variación de entropía de un mol de sustancia si es calentada desde 10°C hasta 800°C a través de la isóbara de 3 [atm]. Considere que C_p no depende de la temperatura.

P1 $K_p = 2,3 \times 10^2 \gg 1 \Rightarrow \alpha \approx 1$



$n_t = 3-x$

* ΔG se optimiza (es mínima) en el equilibrio

$$\Rightarrow K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \cdot P_{\text{O}_2}} = \frac{X_{\text{NO}_2}^2 \cdot P_t^2}{X_{\text{NO}}^2 \cdot P_t^2 \cdot X_{\text{O}_2} \cdot P_t} = \frac{4x^2 / (3-x)^2}{[4(1-x)^2 / (3-x)^2] \cdot [(1-x) / (3-x)]}$$

$$\Rightarrow K_p = \frac{x^2(3-x)}{P_t \cdot (1-x)^3}$$

como $K_p \gg 1 \Rightarrow \alpha = \frac{x}{n_0} \approx 1 \quad / \quad n_0 = 1 \Rightarrow x \approx 1$

$$\Rightarrow K_p = \frac{1^2 \cdot (3-1)}{P_t \cdot (1-x)^3} \Rightarrow K_p \cdot P_t (1-x)^3 = 2$$

$$\therefore \boxed{x = 1 - \sqrt[3]{\frac{2}{P_t \cdot K_p}}}$$

P2

• Clausius-Clapeyron (para eq. sól-sól):

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta \bar{V}} \Rightarrow dP = \underbrace{\left(\frac{\Delta H}{\Delta \bar{V}} \right)}_{\text{estandar}} \cdot \frac{dT}{T} \quad / \int$$

$$\Rightarrow P_2 - P_1 = \left(\frac{\Delta H}{\Delta \bar{V}} \right) \ln \left(\frac{T_2}{T_1} \right)$$

• Calculamos ΔH :

$$\rightarrow \text{En equilibrio } \Delta S = \frac{\Delta H}{T} \Rightarrow \Delta H = T \Delta S$$

• Calculamos ΔS :

$$\rightarrow \Delta S = S_{\text{blanco}} - S_{\text{gris}} = 51,2 - 42,4 = 8,8 \left[\frac{\text{J}}{\text{mol} \cdot \text{K}} \right] \times \frac{0,082 \left[\frac{\text{et} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right]}{8,314 \left[\frac{\text{J}}{\text{mol} \cdot \text{K}} \right]} = 0,0868 \left[\frac{\text{et} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right]$$

$$\Rightarrow \Delta H = T \Delta S = 291 \left[\text{K} \right] \cdot 0,0868 \left[\frac{\text{et} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right] = \boxed{25,26 \left[\frac{\text{et} \cdot \text{atm}}{\text{mol}} \right]}$$

• Calculamos $\Delta \bar{V}$:

$$\rightarrow \Delta \bar{V} = \bar{V}_{\text{blanco}} - \bar{V}_{\text{gris}} = P_H \left[\frac{\text{et}}{\text{mol}} \right] \left(\frac{1}{P_{\text{blanco}}} - \frac{1}{P_{\text{gris}}} \right) \left[\frac{\text{et}}{\text{et}} \right]$$

$$\Rightarrow \Delta \bar{V} = 118 \left[\frac{\text{et}}{\text{mol}} \right] \left(\frac{1}{7280} - \frac{1}{5750} \right) \left[\frac{\text{et}}{\text{et}} \right] = \boxed{-0,0043 \left[\frac{\text{et}}{\text{mol}} \right]}$$

• Ec. cl-cl:

$$300 - 1 \text{atm} \quad \frac{25,26 \left[\frac{\text{et} \cdot \text{atm}}{\text{mol}} \right]}{-0,0043 \left[\frac{\text{et}}{\text{mol}} \right]} \ln \left(\frac{T_2}{291} \right)$$

$$\therefore \boxed{T_2 = 276,8 \left[\text{K} \right]}$$

P3) • Determinai si $\Delta G_{\text{rxn}}(85^\circ\text{C}) < 0$

• $\Delta G(85^\circ\text{C}) = \Delta G^\circ(85^\circ\text{C}) + RT \ln Q$ / $Q = \left(\frac{P_{\text{O}_2}^{1/2}}{P_{\text{Cl}_2}}\right)$

• Calculamos $\Delta G^\circ(85^\circ\text{C})$

$\Delta G^\circ(85) = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$ / ΔH° y ΔS° des. cont^o

$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ(\text{CaCl}_2) + \frac{1}{2} \Delta H^\circ(\text{O}_2) - \Delta H^\circ(\text{CaO}) - \Delta H^\circ(\text{Cl}_2)$
 $= -795,8 - (-634,92) = -160,88 \text{ [kJ/mol]}$

$\Delta S^\circ_{\text{rxn}} = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-160,88 - \Delta G^\circ(25^\circ\text{C})}{298}$

• Calculamos $\Delta G^\circ(25^\circ\text{C})$

$\Delta G^\circ_{\text{rxn}}(25^\circ\text{C}) = \Delta G^\circ_f(\text{CaCl}_2) - \Delta G^\circ_f(\text{CaO})$

• Calculamos $\Delta G^\circ_f(\text{CaCl}_2)$

$\Delta G^\circ_f(\text{CaCl}_2) = \Delta H^\circ_f(\text{CaCl}_2) - T \Delta S^\circ_f(\text{CaCl}_2)$

• Calculamos $\Delta S^\circ_f(\text{CaCl}_2)$ a partir de $\text{Ca}(s) + \text{Cl}_2(g) \rightarrow \text{CaCl}_2(s)$

$\Delta S^\circ_f(\text{CaCl}_2) = -S^\circ(\text{Ca}) - S^\circ(\text{Cl}_2) + S^\circ(\text{CaCl}_2)$
 $= 104,62 - 41,6 - 223,08 = -16,1 \text{ [J/K}\cdot\text{mol]}$

$$\Rightarrow \Delta G_f^\circ(\text{aqlz}) = -795,8 - 298 \cdot (-0,1001) = -748,08 \left[\frac{\text{kJ}}{\text{mol}} \right]$$

$$\Rightarrow \Delta G_{\text{rxn}}^\circ(25^\circ\text{C}) = -748,08 - (-603,3) = -144,78 \left[\text{kJ/mol} \right]$$

$$\Rightarrow \Delta S_{\text{rxn}}^\circ = \frac{-160,88 - (-144,78)}{298} = -0,05401 \left[\frac{\text{kJ}}{\text{K} \cdot \text{mol}} \right]$$

$$\Rightarrow \Delta G_{\text{rxn}}^\circ(85^\circ\text{C}) = -160,88 - 358 \cdot (-0,05401) = -141,54 \left[\text{kJ/mol} \right]$$

$$\Rightarrow \Delta G_{\text{rxn}}(85^\circ\text{C}) = -141,54 + 8,314 \times 10^{-3} \cdot 358 \ln\left(\frac{0,2^{1/2}}{0,8}\right)$$

$$\Rightarrow \boxed{\Delta G_{\text{rxn}}(85^\circ\text{C}) = -143,27 \left[\text{kJ/mol} \right]}$$

< 0

∴ es espontánea //

P4)

1º encontramos pts. triple igualando curvas (s-v) y (l-v):

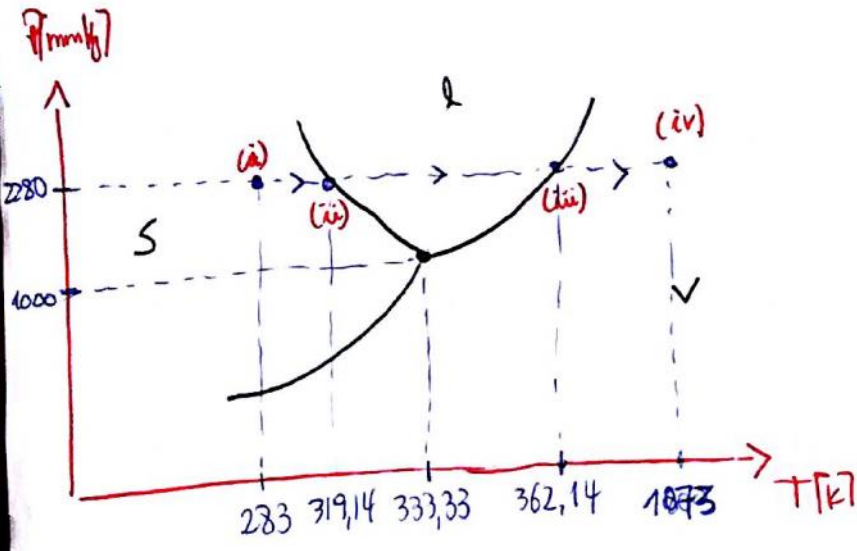
$$\Rightarrow 30,5 - \frac{2500}{T} = 7,5 - \frac{1500}{T} \Rightarrow$$

$$T_t = 333,33 \text{ [K]}$$

$$P_t = 2000 \text{ [mmHg]}$$

• Pto inicial: 3 atm (2280 [mmHg])
10°C = 283 K

• Pto final: 3 atm (2280 [mmHg])
800°C = 1073 K



• buscamos el cambio fase a 3 atm:

(1) $\log(2280) = 7,5 - 1500/T_v \Rightarrow T_v = 362,14 \text{ [K]} \text{ (l-v)}$

(2) $3 = 238,4 - 40,816 \cdot \ln(T_f) \Rightarrow T_f = 319,7 \text{ [K]} \text{ (s-l)}$

• calculamos ΔS de proceso:

$i \rightarrow ii$ $\Delta S_1 = mC \ln\left(\frac{T_2}{T_1}\right) = 1 \text{ [mol]} \cdot 0,08 \left[\frac{\text{cal}}{\text{g} \cdot \text{K}} \right] \cdot 400 \left[\frac{\text{g}}{\text{mol}} \right] \ln\left(\frac{319,14}{283}\right) = 3,9 \left[\frac{\text{cal}}{\text{K}} \right]$

$ii \rightarrow iii$ $\Delta S_2 = 1 \cdot 0,085 \cdot 400 \cdot \ln\left(\frac{362,14}{319,7}\right) = 4,238 \left[\frac{\text{cal}}{\text{K}} \right]$

$iii \rightarrow iv$ $\Delta S_3 = mC_p \ln\left(\frac{T_2}{T_1}\right) - mR \ln\left(\frac{P_2}{P_1}\right) = 1 \text{ [mol]} \cdot 7 \left[\frac{\text{cal}}{\text{mol} \cdot \text{K}} \right] \cdot \ln\left(\frac{1073}{362,14}\right) = 7,603 \left[\frac{\text{cal}}{\text{K}} \right]$

• Calculamos ΔS de cambios de fase, donde

$$\Delta S = \frac{\Delta H}{T} \quad \text{y} \quad \frac{d \ln P}{d(1/T)} = \frac{-\Delta H}{R}$$

ii) (l-v) $\left[\frac{d \log P}{d(1/T)} = \frac{d \ln P}{\ln(10)} \cdot \frac{1}{d(1/T)} = \frac{1}{2,3} \cdot \frac{d \ln P}{d(1/T)} \right]$

derivamos curva (l-v) c/r a (1/T):

$$\frac{d \log P}{d(1/T)} = \frac{1}{2,3} \cdot \frac{d \ln P}{d(1/T)} = -1500 \quad (\text{del gráfico})$$

$$\Rightarrow \frac{d \ln P}{d(1/T)} = -3450 = \frac{-\Delta H_v}{R} \Rightarrow \Delta H_v = 3450 \cdot 1,987 = \underline{6855,15 \text{ cal/mol}}$$

$$\Rightarrow \Delta S_v = \frac{6855,15}{362,14} = \underline{+18,929 \text{ cal/K}}$$

iii) (s-l) \rightarrow derivamos curva (s-v)

$$\Delta H_f = \Delta H_s - \Delta H_v \quad \Rightarrow \quad \frac{d \log P}{d(1/T)} = \frac{1}{2,3} \cdot \frac{d \ln P}{d(1/T)} = -2500 \Rightarrow \frac{d \ln P}{d(1/T)} = -7500 = \frac{-\Delta H_s}{R}$$

$$\Rightarrow \Delta H_s = 14902,5 \text{ [cal]} \quad \Rightarrow \quad \Delta H_f = 14902,5 - 6855,15 = \underline{8047,35 \text{ [cal]}}$$

$$\Rightarrow \Delta S_f = \frac{8047,35}{319,7} = \underline{25,17}$$

$$\therefore \Delta S_t = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_f + \Delta S_v$$