Propriedades de Misturas

Parte 2
<table>
<thead>
<tr>
<th>Substance</th>
<th>Chemical Formula</th>
<th>$M$ (kg/kmol)</th>
<th>$T_c$ (K)</th>
<th>$p_c$ (bar)</th>
<th>$Z_c = \frac{p_c V_c}{RT_c}$</th>
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Exemplo: cálculo de M do ar seco

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<th>Component</th>
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<tr>
<td>Neon, helium, methane, and others</td>
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\[
M = \sum y_i M_i \approx 0.78M_{N_2} + 0.21M_{O_2} + 0.0093M_{Ar} + 0.0003M_{CO_2} \approx 0.78 \times 28 + 0.21 \times 32 + 0.0093 \times 40 + 0.0003 \times 44 = 28.97 \text{kg/kmol}
\]
Exemplo

• A análise molar de um certo produto gasoso é 8% CO\(_2\), 11% de H\(_2\)O, 7% de O\(_2\) e 74% de N\(_2\). Determine: (a) a massa molecular da mistura; (b) a composição em termos de frações mássicas.

• (a) \(M = \sum y_i M_i \approx 0,08 M_{CO2} + 0,11 M_{H2O} + 0,07 M_{O2} + 0,74 M_{N2} = 28,46 \text{kg/kmol}\)

• (b) \(n_i = \frac{m_i}{M_i}\) => \(m_i = n_i M_i\)

\(m_{fi} = \frac{m_i}{m}\) => \(m_{fi} = \frac{n_i M_i}{nM} = y_i \frac{M_i}{M}\)
Assim:

• $mf_{CO_2} = 12,37\%$
• $mf_{H_2O} = 6,96\%$
• $mf_{O_2} = 7,87\%$
• $mf_{N_2} = 72,80\%$
Exemplo

• Uma mistura de gases tem a seguinte composição galvimétrica: 10% H\(_2\), 60% N\(_2\) e 30% CO\(_2\). Determine: (a) as frações molares de cada componente; (b) a massa molecular da mistura.

• (a) \( m_{fi} = \frac{m_i}{m} \) => \( m_i = m_{fi} \cdot m \)

\[
\frac{m_i}{M_i} = \frac{mf_i \cdot m}{M_i}
\]

\[
y_i = \frac{n_i}{n} = \frac{mf_i \cdot m/M_i}{\sum (mf_i \cdot m/M_i)} = \frac{mf_i \cdot m/M_i}{m \sum (mf_i/M_i)} = \frac{mf_i/M_i}{\sum (mf_i/M_i)}
\]
Exemplo (continuação)

Assim

• \( y_{H2} = 63,9\% \)
• \( y_{N2} = 27,4\% \)
• \( y_{CO2} = 8,7\% \)

• (b) \( M = \sum y_i M_i = 0,639 M_{H2} + 0,274 M_{N2} + 0,087 M_{CO2} = 12,79 \text{ kg/kmol} \)
Avaliação de propriedades em processos

- Para poder avaliar processos termodinâmicos envolvendo misturas:
  - Transporte de massa, energia e aplicação 2ª Lei
  - Para processos não reativos, mesmos princípios
  - Diferença: é preciso avaliar propriedades da mistura com base em seus componentes
Processos com misturas a composição CTE

State 1

\[(n_1, n_2, \ldots, n_j)\]

at

\[T_1, p_1\]

State 2

\[(n_1, n_2, \ldots, n_j)\]

at

\[T_2, p_2\]

\[U_1 = \sum_{i=1}^{j} n_i \bar{u}_i(T_1)\]

\[H_1 = \sum_{i=1}^{j} n_i \bar{h}_i(T_1)\]

\[S_1 = \sum_{i=1}^{j} n_i \bar{s}_i(T_1, p_{i1})\]

\[U_2 = \sum_{i=1}^{j} n_i \bar{u}_i(T_2)\]

\[H_2 = \sum_{i=1}^{j} n_i \bar{h}_i(T_2)\]

\[S_2 = \sum_{i=1}^{j} n_i \bar{s}_i(T_2, p_{i2})\]
Processos com misturas a composição CTE

\[ U_2 - U_1 = \sum_{i=1}^{j} n_i [\bar{u}_i(T_2) - \bar{u}_i(T_1)] \]

\[ H_2 - H_1 = \sum_{i=1}^{j} n_i [\bar{h}_i(T_2) - \bar{h}_i(T_1)] \]

\[ S_2 - S_1 = \sum_{i=1}^{j} n_i [\bar{s}_i(T_2, p_{i2}) - \bar{s}_i(T_1, p_{i1})] \]

\[ \Delta \bar{u} = \sum_{i=1}^{j} y_i [\bar{u}_i(T_2) - \bar{u}_i(T_1)] \]

\[ \Delta \bar{h} = \sum_{i=1}^{j} y_i [\bar{h}_i(T_2) - \bar{h}_i(T_1)] \]

\[ \Delta \bar{s} = \sum_{i=1}^{j} y_i [\bar{s}_i(T_2, p_{i2}) - \bar{s}_i(T_1, p_{i1})] \]
Processos com misturas a composição CTE

• Estas eqs. fornecem variações da mistura entre 1 e 2 com base na variação de cada componente

• As propriedades em 1 e 2 de cada componente podem ser obtidas de tabelas de propriedades
  • $\tilde{u}_i$ e $\tilde{h}_i$ são funções apenas de $T$
    • Há tabelas onde são diretamente lidas
  • $\tilde{s}_i$ é função de $T$ e de $P_i$
  • Para gás perfeito:

\[
\Delta \tilde{s}_i = \tilde{s}_i^\circ(T_2) - \tilde{s}_i^\circ(T_1) - \bar{R} \ln \frac{p_{i2}}{p_{i1}}
\]

• E como, para composição cte entre 1 e 2

\[
\Delta \tilde{s}_i = \tilde{s}_i^\circ(T_2) - \tilde{s}_i^\circ(T_1) - \bar{R} \ln \frac{p_2}{p_1}
\]
Processos com misturas a composição CTE

- E agora pode ser calculado a partir de dados tabelados
- Finalmente, assumindo calores específicos ctes

\[
\Delta \bar{u} = \bar{c}_v(T_2 - T_1), \quad \Delta \bar{u}_i = \bar{c}_{v,i}(T_2 - T_1)
\]
\[
\Delta \bar{h} = \bar{c}_p(T_2 - T_1), \quad \Delta \bar{h}_i = \bar{c}_{p,i}(T_2 - T_1)
\]
\[
\Delta \bar{s} = \bar{c}_p \ln \frac{T_2}{T_1} - \bar{R} \ln \frac{p_2}{p_1}, \quad \Delta \bar{s}_i = \bar{c}_{p,i} \ln \frac{T_2}{T_1} - \bar{R} \ln \frac{p_2}{p_1}
\]
<table>
<thead>
<tr>
<th>T (K)</th>
<th>h (kJ/kg)</th>
<th>u (kJ/kg)</th>
<th>s° (kJ/kg · K)</th>
<th>( p_r )</th>
<th>( v_r )</th>
<th>T (K)</th>
<th>h (kJ/kg)</th>
<th>u (kJ/kg)</th>
<th>s° (kJ/kg · K)</th>
<th>( p_r )</th>
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Exemplo

- Uma mistura de 0,3 kg de CO₂ e 0,2 kg de N₂ é comprimida de 1 bar e 300 K a 3 bars seguindo um processo politrópico para o qual n=1,25. Determine: (a) a temperatura final; (b) o trabalho; (c) a transferência de calor; (d) a variação de entropia da mistura.
Exemplo (continuação)

Processo politrópico:

• (a)

\[ T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{(n-1)/n} = 300 \left( \frac{3}{1} \right)^{0.2} = 374 \text{ K} \]

• (b)

\[ W = \int_{1}^{2} p \, dV = \frac{p_2 V_2 - p_1 V_1}{1 - n} = \frac{m (\bar{R}/M)(T_2 - T_1)}{1 - n} \]

onde: \( M = \frac{m}{n} \)

\[ m = 0.3 + 0.2 = 0.5 \text{ kg} \]

\[ n_{\text{CO}_2} = \frac{0.3}{44} = 0.0068 \text{ kmol} \]

\[ n_{\text{N}_2} = \frac{0.2}{28} = 0.0071 \text{ kmol} \]

\[ \Rightarrow M = 35.97 \]
Finalmente:

\[
W = (0.5 \text{ kg}) \left( \frac{8.314 \text{ kJ}}{35.97 \text{ kg} \cdot ^\circ \text{K}} \right) \left( 374 \text{ K} - 300 \text{ K} \right) \frac{1}{1 - 1.25} = -34.21 \text{ kJ}
\]

- (c) \[Q = \Delta U + W\]

onde

\[
\Delta U = n_{\text{CO}_2} \left[ \bar{u}_{\text{CO}_2}(T_2) - \bar{u}_{\text{CO}_2}(T_1) \right] + n_{\text{N}_2} \left[ \bar{u}_{\text{N}_2}(T_2) - \bar{u}_{\text{N}_2}(T_1) \right]
\]

Table A-23 \[\Rightarrow \Delta U = 26.3 \text{ kJ}\]

\[Q = +26.3 - 34.21 = -7.91 \text{ kJ}\]
Exemplo (continuação)

- (d) \[ \Delta S = n_{\text{CO}_2} \Delta s_{\text{CO}_2} + n_{\text{N}_2} \Delta s_{\text{N}_2} \]

onde \[ \Delta s_i = s_i^0(T_2) - s_i^0(T_1) - R \ln \frac{p_2}{p_1} \]

Table A-23 => \[ \Delta S = 0.0068 \left(222.475 - 213.915 - 8.314 \frac{3}{1} \right) \]

\[ + 0.0071 \left(198.105 - 191.682 - 8.314 \frac{3}{1} \right) \]

\[ = -0.0231 \text{ kJ/K} \]
Exemplo

• Uma mistura de CO$_2$ e de O$_2$ com frações molares 0,8 e 0,2, respectivamente, se expande isentropicamente e em regime permanente em um bocal, de 700K, 5bars e 3m/s, a uma pressão de saída de 1 bar. Determine: (a) a temperatura na saída; (b) as variações de entropia do CO$_2$ e do O$_2$; (c) a velocidade na saída.
Exemplo (continuação)

• (a) : isentrópico => \( \bar{s}_2 - \bar{s}_1 = y_{O_2} \Delta \bar{s}_{O_2} + y_{CO_2} \Delta \bar{s}_{CO_2} = 0 \)

\[
y_{O_2} \left[ \bar{s}_{O_2}(T_2) - \bar{s}_{O_2}(T_1) - \frac{p_2}{p_1} \ln \frac{p_2}{p_1} \right] + y_{CO_2} \left[ \bar{s}_{CO_2}(T_2) - \bar{s}_{CO_2}(T_1) - \frac{p_2}{p_1} \ln \frac{p_2}{p_1} \right] = 0
\]

\[
y_{O_2} \bar{s}_{O_2}^o(T_2) + y_{CO_2} \bar{s}_{CO_2}^o(T_2) = y_{O_2} \bar{s}_{O_2}^o(T_1) + y_{CO_2} \bar{s}_{CO_2}^o(T_1) + (y_{O_2} + y_{CO_2}) \frac{R}{p_1} \ln \frac{p_2}{p_1}
\]

Table A-23

Nos fornece os \( s^o \) no estado 1, de forma que ficamos com:

\[
0.2\bar{s}_{O_2}^o(T_2) + 0.8\bar{s}_{CO_2}^o(T_2) = 233.42 \text{ kJ/kmol} \cdot \text{K}
\]

E \( T_2 \) pode ser encontrado de forma iterativa, comparando LHS e RHS com Tab. A23

at \( T = 510 \text{ K} \): \( 0.2(221.206) + 0.8(235.700) = 232.80 \)

at \( T = 520 \text{ K} \): \( 0.2(221.812) + 0.8(236.575) = 233.62 \)

Interpolando: \( T_2 = 517.6 \text{ K} \).
Exemplo (continuação)

• (b)

\[
\Delta s_{O_2} = s_{O_2}^o(T_2) - s_{O_2}^o(T_1) - R \ln \frac{p_2}{p_1}
\]

\[
\Delta s_{CO_2} = s_{CO_2}^o(T_2) - s_{CO_2}^o(T_1) - R \ln \frac{p_2}{p_1}
\]

Utilizando Tab. A23:

\[
\Delta s_{O_2} = 3.69 \text{ kJ/kmol} \cdot \text{K}
\]

\[
\Delta s_{CO_2} = -0.92 \text{ kJ/kmol} \cdot \text{K}
\]

• (c) aplicando a eq. da energia:

\[
0 = h_1 - h_2 + \frac{V_1^2 - V_2^2}{2}
\]

\[\Rightarrow V_2 = \sqrt{V_1^2 + 2(h_1 - h_2)}\]

Onde:

\[
h_1 - h_2 = \frac{\bar{h}_1 - \bar{h}_2}{M} = \frac{1}{M} [y_{O_2}(\bar{h}_1 - \bar{h}_2)_{O_2} + y_{CO_2}(\bar{h}_1 - \bar{h}_2)_{CO_2}]
\]
Exemplo (continuação)

Para M:

\[ M = 0.8(44) + 0.2(32) = 41.6 \text{ kg/kmol} \]

E utilizando a Tab. A23

\[ h_1 - h_2 = \frac{1}{41.6} \left[ 0.2(21.184 - 15.320) + 0.8(27.125 - 18.468) \right] = 194.7 \text{ kJ/kg} \]

Finalmente:

\[ V_2 = \sqrt{\left(3 \frac{\text{m}}{\text{s}}\right)^2 + 2 \left(194.7 \frac{\text{kJ}}{\text{kg}}\right) \frac{1 \text{ kg \cdot m/s}^2}{1 \text{ N}} \frac{10^3 \text{ N \cdot m}}{1 \text{ kJ}}} = 624 \text{ m/s} \]
Misturando gases ideais

- Gases com composição variando, porém sem reação química
- Os gases estão inicialmente separados, e são misturados
  - Esta mistura é um processo irreversível
- 3 fatores contribuem para produção de entropia:
  - Temperaturas dos gases inicialmente diferentes
  - Pressões dos gases inicialmente diferentes
  - Gases com composições iniciais distintas
Exemplo

- 2 tanques rígidos e isolados estão conectados por uma válvula. Inicialmente, tem-se 0,79 kmol de N\textsubscript{2} a 2 bars e 250K em um dos tanques. O outro tanque contém 0,21 kmol de O\textsubscript{2} a 1 bar e 300K. A válvula é aberta e um processo de mistura sem troca de calor ou trabalho com o ambiente externo ao tanque acontece, até que um estado de equilíbrio é atingido. Determine: (a) a temperatura final de mistura; (b) a pressão final da mistura; (c) a produção de entropia neste processo.
Exemplo (continuação)

• (a) Da primeira lei:

Onde

\[ U_2 - U_1 = 0 \]

\[ U_1 = n_{N_2} \overline{u}_{N_2}(T_{N_2}) + n_{O_2} \overline{u}_{O_2}(T_{O_2}) \]

\[ U_2 = n_{N_2} \overline{u}_{N_2}(T_2) + n_{O_2} \overline{u}_{O_2}(T_2) \]

Logo

\[ n_{N_2} \overline{u}_{N_2}(T_2) - \overline{u}_{N_2}(T_{N_2}) \right\} + n_{O_2} \overline{u}_{O_2}(T_2) - \overline{u}_{O_2}(T_{O_2}) = 0 \]

E \( T_2 \) pode ser encontrado de forma iterativa. Alternativamente, podemos considerar que \( c_v \) pouco varia, Neste caso:

\[ n_{N_2} \overline{c}_{v,N_2}(T_2 - T_{N_2}) + n_{O_2} \overline{c}_{v,O_2}(T_2 - T_{O_2}) = 0 \]

\[ T_2 = \frac{n_{N_2} \overline{c}_{v,N_2} T_{N_2} + n_{O_2} \overline{c}_{v,O_2} T_{O_2}}{n_{N_2} \overline{c}_{v,N_2} + n_{O_2} \overline{c}_{v,O_2}} \]

Avaliando \( c_v \) da Tab. A20:

\[ T_2 = 261^\circ K \]
Exemplo (continuação)

• (b) observando que o volume total é o volume dos 2 tanques:

\[ V = \frac{n_{N_2} RT_{N_2}}{p_{N_2}} + \frac{n_{O_2} RT_{O_2}}{p_{O_2}} \]

Onde, no estado inicial temos:

\[ p_{O_2} = 1 \text{ atm} \quad p_{N_2} = 2 \text{ atm} \]

e o estado final pode ser calculado de \( P_2 = \frac{nRT}{V} \), onde V se conserva:

\[ P_2 = \frac{(n_{N_2} + n_{O_2}) T_2}{\left( \frac{n_{N_2} T_{N_2}}{p_{N_2}} + \frac{n_{O_2} T_{O_2}}{p_{O_2}} \right)} = 1.62 \text{ bars} \]

• (c) para processo adiabático:

\[ S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right)_b + \sigma \]
Exemplo (continuação)

Onde

\[ S_1 = n_{N_2} \bar{s}_{N_2}(T_{N_2}, p_{N_2}) + n_{O_2} \bar{s}_{O_2}(T_{O_2}, p_{O_2}) \]
\[ S_2 = n_{N_2} \bar{s}_{N_2}(T_2, y_{N_2}p_2) + n_{O_2} \bar{s}_{O_2}(T_2, y_{O_2}p_2) \]

Logo:

\[
\sigma = n_{N_2}[\bar{s}_{N_2}(T_2, y_{N_2}p_2) - \bar{s}_{N_2}(T_{N_2}, p_{N_2})] \\
+ n_{O_2}[\bar{s}_{O_2}(T_2, y_{O_2}p_2) - \bar{s}_{O_2}(T_{O_2}, p_{O_2})]
\]

\[
\sigma = n_{N_2}\left(\bar{c}_{p,N_2} \ln \frac{T_2}{T_{N_2}} - \bar{R} \ln \frac{y_{N_2}p_2}{p_{N_2}}\right) + n_{O_2}\left(\bar{c}_{p,O_2} \ln \frac{T_2}{T_{O_2}} - \bar{R} \ln \frac{y_{O_2}p_2}{p_{O_2}}\right)
\]

E podemos achar \( c_p \):

\[ c_p = c_v + R \]

\[ c_{p,N_2} = 29.13 \frac{kJ}{kmol \cdot K} \]
\[ c_{p,O_2} = 29.30 \frac{kJ}{kmol \cdot °K} \]

Finalmente:

\[ \sigma = 5.0 \text{ kJ/°K} \]