Heat capacity for moist porous solid

1 Pore contents

1.1 Mass of vapour

According to the ideal gas law, the number of moles of vapour n is

$$n = \frac{p_0 V}{R T_0}$$

And since the molar mass M is the mass per mole,

$$m_{s_0} = M n$$
$$= \frac{M V p_0}{R T_0}$$

1.2 Mass of vapour and liquid water

The mass of vapour is

$$m_s(T) = M n$$
$$= \frac{M V p}{R T}$$
$$= \frac{M V}{R T} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

By conservation of mass,

$$m_s(T) + m_w(T) = m_{s_0} + m_{w_0}$$
$$m_w(T) = m_{s_0} + m_{w_0} - m_s(T)$$
$$= \frac{M V p_0}{R T_0} + m_{w_0} - \frac{M V}{R T} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

1.3 Vapour mass change

$$m_s(T) = \frac{M V}{R T} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$
$$\frac{d m_s(T)}{d T} = \frac{d}{d T}\left(\frac{M V}{R T} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}\right)$$
$$= -\frac{M V}{R T^2} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + \frac{M V}{R T} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} \frac{M L}{R T^2}$$
$$= \frac{M V}{R T^2} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}\left(\frac{M L}{R T} - 1\right)$$

Hence

$$\Delta m_s(T) = \frac{M V}{R T^2} p_0 e^{\frac{M L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}\left(\frac{M L}{R T} - 1\right)\Delta T$$

1.4 Heat capacity of pore

The number of moles of vapour is

$$
\begin{aligned}
n_s(T) &= \frac{m_s(T)}{M} \\
&= \frac{V}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}
\end{aligned}
$$

The number of moles of liquid water is

$$
\begin{aligned}
n_w(T) &= \frac{m_w(T)}{M} \\
&= \frac{Vp_0}{RT_0} + \frac{m_{w_0}}{M} - \frac{V}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}
\end{aligned}
$$

And the heat capacity is the sum of the heat capacity of the liquid and the heat capacity of the vapour

$$
\begin{aligned}
C_p(T) &= c_w n_w(T) + 3R n_s(T) \\
&= \frac{c_w V p_0}{RT_0} + \frac{c_w m_{w_0}}{M} - \frac{c_w V}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + \frac{3V}{T} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}
\end{aligned}
$$

1.5 Complete evarpouration

The volume of the liquid water is $V_w = \delta V$, hence the mass is $m_{w_0} = \rho_w V_w = \rho_w \delta V$. Then the condition for complete evapouration is that $m_w = 0$ or

$$
\begin{aligned}
m_w(T) &= \frac{MVp_0}{RT_0} + m_{w_0} - \frac{MV}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} \\
0 &= \frac{MVp_0}{RT_0} + \rho_w \delta V - \frac{MV}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} \\
&= \frac{Mp_0}{RT_0} + \rho_w \delta - \frac{M}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}
\end{aligned}
$$

Hence, letting $T = T_1$,

$$
\begin{aligned}
\frac{Mp_0}{RT_0} + \rho_w \delta &= \frac{M}{RT_1} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)} \\
e^{-\frac{ML}{RT_0}} \left(\frac{ML}{RT_0} + \frac{L\rho_w \delta}{p_0}\right) &= \frac{ML}{RT_1} e^{-\frac{ML}{RT_1}} \\
&= 1.305 \times 10^{-4}
\end{aligned}
$$

solving numerically,

$$
\begin{aligned}
\frac{ML}{RT_1} &= 11.38 \\
T_1 &= 438 \text{ K}
\end{aligned}
$$

1.6 Significant terms

We consider the case where $T = T_0$, and $V = 0.1$ cm^3 then

$$C_p(T) = \frac{c_w V p_0}{R T_0} + \frac{c_w m_{w_0}}{M} - \frac{c_w V}{RT} p_0 + \frac{3V}{T} p_0$$

$$\frac{c_w V p_0}{R T_0} = 5.9 \times 10^{-4} \text{ J/K}$$

$$\frac{c_w m_{w_0}}{M} = 6.6 \times 10^{-2} \text{ J/K}$$

$$\frac{c_w V}{RT} p_0 = 5.9 \times 10^{-4} \text{ J/K}$$

$$\frac{3V}{T} p_0 = 3.5 \times 10^{-6} \text{ J/K}$$

As T increase, however, the exponential term grows larger; hence we can keep the two largest terms and get

$$C_p(T) = \frac{c_w m_{w_0}}{M} - \frac{c_w V}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

The first term is the initial heat capacity of water and the second term is the capacity 'lost' due to evapouration. It seems that the vapour does not contribute to the heat capacity and does not contain a lot of water.

1.7 Specific heat capacity

Since the total mass of pore content is always the same (water does not enter/exit the pore), the mass of pore content is

$$m_{s_0} + m_{w_0} = \frac{MV p_0}{R T_0} + \delta \rho_w V$$

and the specific heat capacity is

$$c_p(T) = \frac{C_p(T)}{m_s + m_w}$$

$$= \frac{\frac{c_w V p_0}{R T_0} + \frac{c_w \delta \rho_w V}{M} - \frac{c_w V}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + \frac{3V}{T} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}}{\frac{MV p_0}{R T_0} + \delta \rho_w V}$$

$$= \frac{\frac{c_w p_0}{R T_0} + \frac{c_w \delta \rho_w}{M} - \frac{c_w}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + \frac{3}{T} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}}{\frac{M p_0}{R T_0} + \delta \rho_w}$$

for $T = T_0$,

$$c_p(T_0) = \frac{\frac{c_w \delta \rho_w}{M} + \frac{3}{T_0} p_0}{\frac{M p_0}{R T_0} + \delta \rho_w}$$

$$= 231.1 \text{ J/gK}$$

When $T > T_1$, there is no more water left and the terms that depend on c_w sum to 0. Hence

$$c_p(T_1) = \frac{\frac{3}{T_1} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)}}{\frac{M p_0}{R T_0} + \delta \rho_w}$$

$$= 3.10 \text{ J/gK}$$

for $T > T_1$, since there is no further change to the composition of the pore (all of it is vapour), hence $c_p = 3.10$ J/gK

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2 Porous solid

2.1 Specific heat capacity

The mass of the solid body

$$m_S = (1-\xi)\rho_S V_t$$

where V_t is the total body volume. Also,

$$V = \xi V_t$$

Hence, if H_S is the heat capacity of the body,

$$c(T) = \frac{C_p(T) + H_S(T)}{m_s + m_w + m_S}$$

$$= \frac{\frac{c_w \xi V_t p_0}{RT_0} + \frac{c_w \delta \rho_w \xi V_t}{M} - \frac{c_w \xi V_t}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + \frac{3\xi V_t}{T} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + C_S(1-\xi)\rho_S V_t}{\frac{M\xi V_t p_0}{RT_0} + \delta \rho_w \xi V_t + (1-\xi)\rho_S V_t}$$

$$= \frac{\frac{c_w \xi p_0}{RT_0} + \frac{c_w \delta \rho_w \xi}{M} - \frac{c_w \xi}{RT} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + \frac{3\xi}{T} p_0 e^{\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} + C_S(1-\xi)\rho_S}{\frac{M\xi p_0}{RT_0} + \delta \rho_w \xi + (1-\xi)\rho_S}$$

2.2 Numerical value

$$c_p(T_0) = 2591 \text{ J/kgK}$$
$$c_p(T_1) = 111 \text{ J/kgK}$$

For $T > T_1$, since the composition of the pore doesn't change, c_p is still 111 J/kgK

2.3 Graph