Exercise S7

wednesday 20 mei 2020 20:47

$\boxed{Pv = RT}$

a)

$$PV = nRT = \frac{N}{N_A} RT = N k_B T$$

$$\boxed{R = k_B N_A}$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} \; ?$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,T} = \frac{P}{T}$$

$$S = \int \frac{P}{T} dV\Big|_{N,T} = \frac{1}{T}\int p\, dV\Big|_{N,T} = \frac{1}{T}\int \frac{N k_B T}{V} dV\Big|_{N,T}$$

$$= N k_B \int \frac{1}{V} dV\Big|_{N,T}$$

$$= N k_B \ln\left(\frac{V}{V_0(N,T)}\right)$$

Because S has to be extensive, $V_0 = N\, v(T)$

$$= N k_B \ln\left(\frac{V}{N\, v(T)}\right)$$

$$= -k_B N \ln\left(\frac{N}{V} v(T)\right)$$

b)

$$C_V = 3 k_B N/2 = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$$

$$\frac{3 k_B N}{2T} = \left(\frac{\partial}{\partial T} -k_B N \ln\left(\frac{N}{V} v(T)\right)\right)_{N,V}$$

$$-\frac{3}{2T} = \frac{\frac{N}{V}}{\frac{N}{V} v(T)} \left(\frac{\partial v(T)}{\partial T}\right)_{N,V}$$

$$-\frac{3}{2T} = \frac{1}{v(T)} \left(\frac{\partial v(T)}{\partial T}\right)_{N,V}$$

$$\frac{3}{2T} = -\frac{\partial \ln v}{\partial T}$$

$$\boxed{\frac{1}{f(T)} \frac{\partial f(T)}{\partial T} = \frac{\partial \ln(f(T))}{\partial T}}$$

Why?

Chain rule! (reversed)

$$\partial \ln(v) = -\frac{3}{2} \partial \ln(T)$$

$$\int d\ln(v) = \int -\frac{3}{2} d\ln(T)$$

$$\ln(v) = -\frac{3}{2}\ln(T) + C'$$

$$\ln(v) = -\frac{3}{2}\ln(T) + \ln(C)$$

$$v = e^{\ln C T^{-\frac{3}{2}}}$$

$$v = C T^{-\frac{3}{2}}$$

$$v(T) \propto T^{-\frac{3}{2}}$$

c)

$$S = k_B \ln W \Rightarrow W \propto e^{\frac{S}{k_B}} \Rightarrow \frac{W}{\Omega} \propto e^{\frac{S}{k_B}} \Rightarrow P \propto e^{\frac{S}{k_B}}$$

$$P \propto e^{\frac{S}{k_B}}$$

from question a: $\frac{S}{k_B} = -N \ln\left(\frac{N}{V} v(T)\right)$

$$= \ln\left(\left(\frac{V}{N v(T)}\right)^N\right) \propto \ln V^N$$

$$P \propto e^{\frac{S}{k_B}} \propto e^{\ln V^N} = V^N$$

$$P(\Delta V) \propto \Delta V^N$$

$$P(V) \propto V^N$$

$$\frac{P(\Delta V)}{P(V)} = \left(\frac{\Delta V}{V}\right)^N$$

d)

$$P(\text{all gas in 1m of 3m}) = \frac{P(\Delta V)}{P(V)} = \left(\frac{\Delta V}{V}\right)^N = \left(\frac{1 \times 100\ m^3}{3 \times 100\ m^3}\right)^N = \frac{1}{3^N}$$

$$N = \frac{pV}{k_B T} = \frac{10^5\ Nm^{-2} \times 300\ m^3}{1.14 \times 10^{-23}\ Nm\,K^{-1} \times 300\ K} = 7 \times 10^{27}$$

Hence, by the ergodic theorem: fraction of time = fraction of ensemble average = probability

$$= \frac{1}{3^{7\times10^{27}}} \approx 2.1 \times 10^{-28}$$

which is 'negligible'