



**MathsNET**

A joined up approach to  
teaching and learning  
mathematics

# The isothermal-isobaric ensemble

---

- Which extensive thermodynamic variables are constrained to have a particular value in the isothermal-isobaric ensemble.
- Give an expression for the probability of being in a microstate in the isothermal-isobaric ensemble
- Give an expression for the isothermal-isobaric partition function
- Give an expression for  $\frac{dS}{k_B}$  for the isothermal-isobaric ensemble that can be obtained using arguments based on statistical mechanics.



**MathsNET**

A joined up approach to  
teaching and learning  
mathematics

# The isothermal-isobaric ensemble

---

- Give an expression for the Lagrange multiplier  $\lambda$  and explain how this result is derived.
- What thermodynamic potential can be calculated from the isothermal-isobaric partition function? How is this done and how is this result derived?
- Explain why:  $1 = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j) - \beta PV(\mathbf{x}_i, \mathbf{p}_i) - \Psi}$
- Now calculate the first derivative of  $1 = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j) - \beta PV(\mathbf{x}_i, \mathbf{p}_i) - \Psi}$  with respect to  $\beta P$  and hence show that  $\langle V \rangle = -\frac{\partial \Psi}{\partial(\beta V)}$



**MathsNET**

A joined up approach to  
teaching and learning  
mathematics

# The isothermal-isobaric ensemble

---

- Calculate the second derivative of  $1 = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j) - \beta PV(\mathbf{x}_i, \mathbf{p}_i) - \Psi}$  with respect to  $\beta P$  and hence show that  $\langle (V - \langle V \rangle)^2 \rangle = \frac{\partial^2 \Psi}{\partial (\beta P)^2}$
- Explain (in your own words) why  $\langle (V - \langle V \rangle)^2 \rangle = -\frac{\partial \Psi}{\partial (\beta P)}$ .
- Use the chain rule to show that:  $\frac{\partial \langle V \rangle}{\partial (\beta P)} = k_B T \frac{\partial \langle V \rangle}{\partial P}$  if  $T$  is constant.
- Use the result you have just arrived at to write an expression that tells you how the isothermal compressibility,  $\kappa_T$ , can be calculated from the fluctuations in the total volume  $\langle (V - \langle V \rangle)^2 \rangle$