Focus 2: The First Law

Internal Energy

Enthalpy

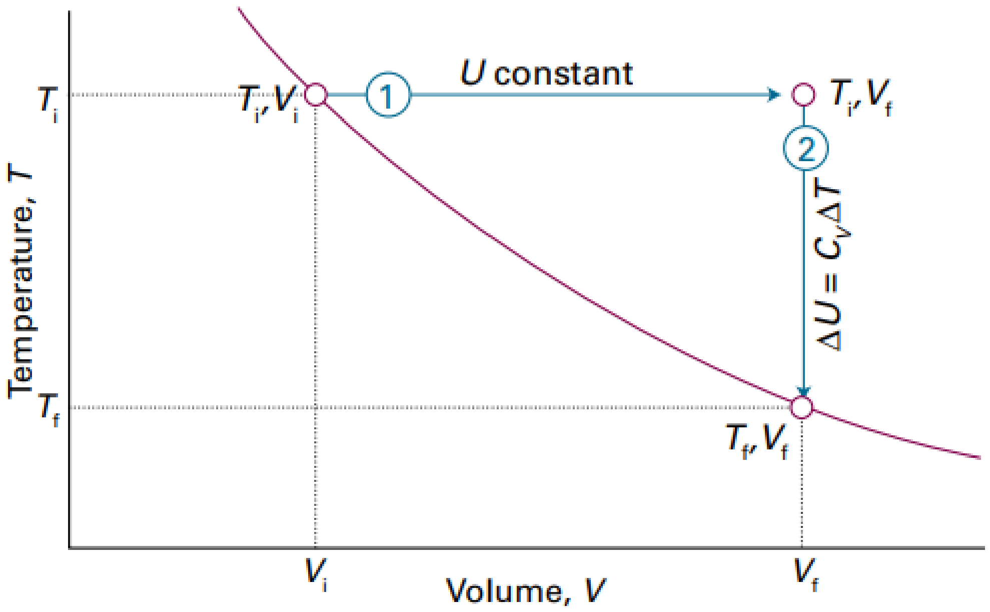
Thermochemistry

State functions

Adiabatic changes

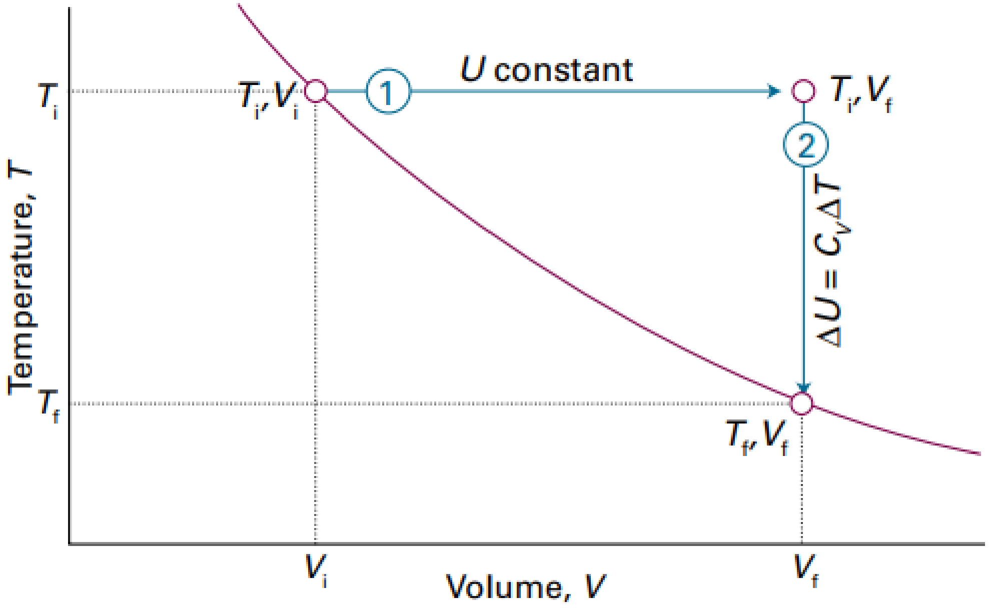
Work in an adiabatic change

Perfect gas



Work in an adiabatic change

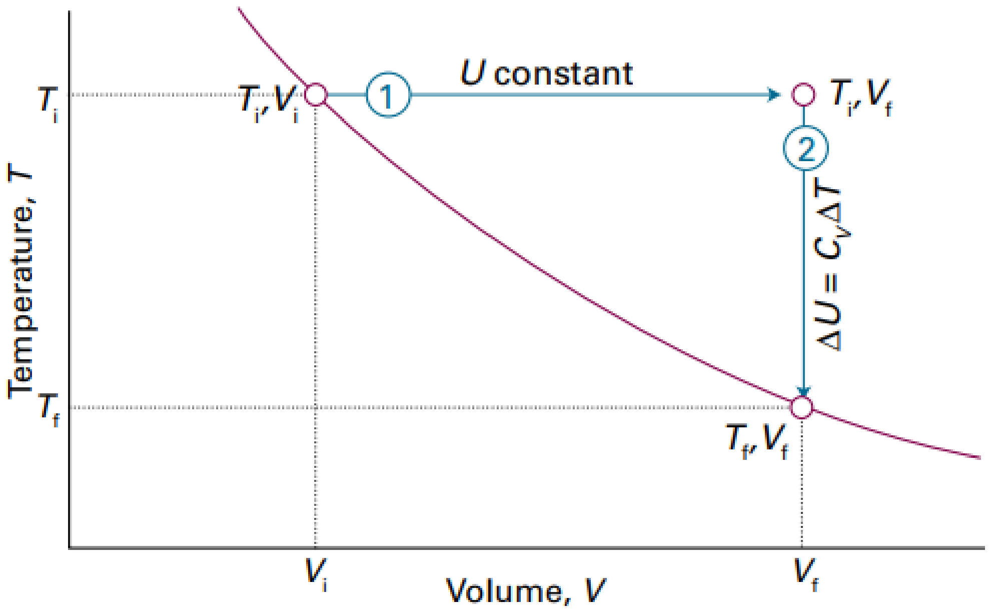
Perfect gas



$$\Delta U = (T_f - T_i)C_V = C_V \Delta T$$

Work in an adiabatic change

Perfect gas



$$\Delta U = (T_f - T_i)C_V = C_V \Delta T$$

$$\Delta U = w_{ad} = C_V \Delta T$$

Temperature change in an adiabatic change (reversible)

$$dw = -pdV$$

to any reversible change

Temperature change in an adiabatic change (reversible)

$$dw = -p dV.$$

to any reversible change

$$dU = C_V dT$$

Temperature change in an adiabatic change (reversible, perfect gas)

$$dw = -p dV$$

to any reversible change

$$dU = C_V dT$$

$$C_V dT = -p dV$$

Temperature change in an adiabatic change (reversible)

$$\mathrm{d}w = -p\mathrm{d}V.$$

to any reversible change

$$\mathrm{d}U = C_V\mathrm{d}T$$

$$C_V\mathrm{d}T = -p\mathrm{d}V$$

$$\frac{C_V\mathrm{d}T}{T} = -\frac{nR\mathrm{d}V}{V}$$

Temperature change in an adiabatic change (reversible)

$$dw = -p\,dV$$

to any reversible change

$$dU = C_V\,dT$$

$$C_V\,dT = -p\,dV$$

$$\frac{C_V\,dT}{T} = -\frac{nR\,dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

Temperature change in an adiabatic change (reversible)

$$dw = -p\,dV$$

to any reversible change

$$dU = C_V\,dT$$

$$C_V\,dT = -p\,dV$$

$$\frac{C_V\,dT}{T} = -\frac{nR\,dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln\frac{T_f}{T_i} = -nR \ln\frac{V_f}{V_i}$$

Temperature change in an adiabatic change (reversible)

$$dw = -p dV$$

$$dU = C_V dT$$

to any reversible change

$$C_V dT = -p dV$$

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

$$\frac{C_V}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

Temperature change in an adiabatic change (reversible)

$$dw = -p dV$$

to any reversible change

$$dU = C_V dT$$

$$C_V dT = -p dV$$

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

$$\frac{C_V}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

$$C_V / nR = C_{V,m} / R$$

Temperature change in an adiabatic change (reversible)

$$dw = -p dV$$

to any reversible change

$$dU = C_V dT$$

$$C_V dT = -p dV$$

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln\frac{T_f}{T_i} = -nR \ln\frac{V_f}{V_i} \qquad \frac{C_V}{nR}\ln\frac{T_f}{T_i} = \ln\frac{V_i}{V_f}$$

$$C_V/nR = C_{V,m}/R = c$$

Temperature change in an adiabatic change (reversible)

$$dw = -p dV$$

to any reversible change

$$dU = C_V dT$$

$$C_V dT = -p dV$$

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

$$\frac{C_V}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

$$C_V/nR = C_{V,m}/R = c$$

$$\ln \left(\frac{T_f}{T_i} \right)^c = \ln \frac{V_i}{V_f}$$

$$\boxed{\ln x^a = a \ln x}$$

Temperature change in an adiabatic change (reversible)

$$dw = -p\,dV$$

to any reversible change

$$dU = C_V dT$$

$$C_V dT = -p\,dV$$

$$\frac{C_V dT}{T} = -\frac{nR\,dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln\frac{T_f}{T_i} = -nR \ln\frac{V_f}{V_i}$$

$$\frac{C_V}{nR} \ln\frac{T_f}{T_i} = \ln\frac{V_i}{V_f}$$

$$C_V/nR = C_{V,m}/R = c$$

$$\ln\left(\frac{T_f}{T_i}\right)^c = \ln\frac{V_i}{V_f}$$

$$\boxed{\ln x^a = a \ln x}$$

$$T_f = T_i\left(\frac{V_i}{V_f}\right)^{1/c} \quad c = C_{V,m}/R$$

Temperature change in an adiabatic change (reversible)

$$dw = -p\,dV$$

to any reversible change

$$dU = C_V\,dT$$

$$C_V\,dT = -p\,dV$$

$$\frac{C_V\,dT}{T} = -\frac{nR\,dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln\frac{T_f}{T_i} = -nR \ln\frac{V_f}{V_i} \qquad \frac{C_V}{nR}\ln\frac{T_f}{T_i} = \ln\frac{V_i}{V_f}$$

$$C_V/nR = C_{V,m}/R = c$$

$$\ln\left(\frac{T_f}{T_i}\right)^c = \ln\frac{V_i}{V_f}$$

$$\ln x^a = a \ln x$$

$$T_f = T_i\left(\frac{V_i}{V_f}\right)^{1/c} \qquad c = C_{V,m}/R$$

$$V_i T_i^c = V_f T_f^c$$

Temperature change in an adiabatic change (reversible)

$$dw = -p\mathrm{d}V$$

to any reversible change

$$\mathrm{d}U = C_V \mathrm{d}T$$

$$C_V \mathrm{d}T = -p\mathrm{d}V$$

$$\frac{C_V \mathrm{d}T}{T} = -\frac{nR\mathrm{d}V}{V}$$

$$C_V \int_{T_\mathrm{i}}^{T_\mathrm{f}} \frac{\mathrm{d}T}{T} = -nR \int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{\mathrm{d}V}{V}$$

$$C_V \ln \frac{T_\mathrm{f}}{T_\mathrm{i}} = -nR \ln \frac{V_\mathrm{f}}{V_\mathrm{i}}$$

$$\frac{C_V}{nR} \ln \frac{T_\mathrm{f}}{T_\mathrm{i}} = \ln \frac{V_\mathrm{i}}{V_\mathrm{f}}$$

$$C_V/nR = C_{V,\mathrm{m}}/R = c$$

$$\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^c = \ln \frac{V_\mathrm{i}}{V_\mathrm{f}}$$

$$\ln x^a = a \ln x$$

$$T_\mathrm{f} = T_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{1/c} \qquad c = C_{V,\mathrm{m}}/R$$

$$V_\mathrm{i} T_\mathrm{i}^c = V_\mathrm{f} T_\mathrm{f}^c$$

$$VT^c = \text{constant.} \qquad c = C_{V,\mathrm{m}}/R$$

Question – Calculate W_{ad}

$$c = C_{V,m} / R$$

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm^3 to 1.00 dm^3. The molar heat capacity of argon at constant volume is 12.47 $J\,K^{-1}\,mol^{-1}$

Question - Calculate W_{ad}

$c = C_{V,m} / R$

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm^3 to 1.00 dm^3. The molar heat capacity of argon at constant volume is 12.47 $J\,K^{-1}\,mol^{-1}$, so $c = 1.501$.

Question - Calculate W_{ad}

$$c = C_{V,\mathrm{m}} / R$$

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm^3 to 1.00 dm^3. The molar heat capacity of argon at constant volume is 12.47 J K^{-1} mol^{-1}, so $c = 1.501$.

$$\Delta U = w_{\mathrm{ad}} = C_V \Delta T$$

Question - Calculate W_{ad}

$$c = C_{V,m} / R$$

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm^3 to 1.00 dm^3. The molar heat capacity of argon at constant volume is 12.47 J K^{-1} mol^{-1}, so $c = 1.501$.

$$\Delta U = w_{ad} = C_V \Delta T$$

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

Question - Calculate W_{ad}

$$c = C_{V,\mathrm{m}} / R$$

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm^3 to 1.00 dm^3. The molar heat capacity of argon at constant volume is 12.47 $\mathrm{J\,K^{-1}\,mol^{-1}}$, so $c = 1.501$.

$$\Delta U = w_{\mathrm{ad}} \quad = C_V \Delta T$$

$$T_{\mathrm{f}} = T_{\mathrm{i}} \left(\frac{V_{\mathrm{i}}}{V_{\mathrm{f}}} \right)^{1/c}$$

$$T_{\mathrm{f}} = (298\,\mathrm{K}) \times \left(\frac{0.50\,\mathrm{dm}^3}{1.00\,\mathrm{dm}^3} \right)^{1/1.501} \quad = 188\,\mathrm{K}$$

Question - Calculate W_{ad}

$$c = C_{V,m} / R$$

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm^3 to 1.00 dm^3. The molar heat capacity of argon at constant volume is 12.47 $J\,K^{-1}\,mol^{-1}$, so $c = 1.501$.

$$\Delta U = w_{ad} = C_V \Delta T = \{(0.020\,\text{mol}) \times (12.47\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\} \times (-110\,\text{K}) = -27\,\text{J}$$

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

$$T_f = (298\,\text{K}) \times \left(\frac{0.50\,\text{dm}^3}{1.00\,\text{dm}^3} \right)^{1/1.501} = 188\,\text{K}$$

Pressure change in an adiabatic process (reversible)

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f}$$

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

Pressure change in an adiabatic change (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i} \right)^{1/c}$$

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i} \right)^{1/c}$$

$$\frac{p_i}{p_f} \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}+1} = 1$$

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i \left(\frac{V_i}{V_f}\right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i}\right)^{1/c}$$

$$\frac{p_i}{p_f}\left(\frac{V_i}{V_f}\right)^{\frac{1}{c}+1} = 1$$

$$\frac{1}{c} + 1 = \frac{1+c}{c}$$

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i} \right)^{1/c}$$

$$\frac{p_i}{p_f} \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}+1} = 1$$

$$\frac{1}{c} + 1 = \frac{1+c}{c}$$

$$= \frac{R + C_{V,m}}{C_{V,m}} \qquad c = C_{V,m} / R$$

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i\left(\frac{V_i}{V_f}\right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i}\right)^{1/c}$$

$$\frac{p_i}{p_f}\left(\frac{V_i}{V_f}\right)^{\frac{1}{c}+1} = 1$$

$$\frac{1}{c} + 1 = \frac{1+c}{c}$$

$$= \frac{R + C_{V,m}}{C_{V,m}} \qquad c = C_{V,m}/R$$

$$= \frac{C_{p,m}}{C_{V,m}} \qquad C_{p,m} - C_{V,m} = R$$

Pressure change in an adiabatic change (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i} \right)^{1/c}$$

$$\frac{p_i}{p_f} \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}+1} = 1$$

$$\frac{1}{c} + 1 = \frac{1+c}{c}$$

$$= \frac{R + C_{V,\mathrm{m}}}{C_{V,\mathrm{m}}} \qquad c = C_{V,\mathrm{m}} / R$$

$$= \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} \qquad C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$$

$$= \gamma$$

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i} \right)^{1/c}$$

$$\frac{p_i}{p_f} \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}+1} = 1$$

$$\frac{1}{c} + 1 = \frac{1+c}{c}$$

$$= \frac{R + C_{V,m}}{C_{V,m}} \qquad c = C_{V,m} / R$$

$$= \frac{C_{p,m}}{C_{V,m}} \qquad C_{p,m} - C_{V,m} = R$$

$$= \gamma$$

$$\frac{p_i}{p_f} \left(\frac{V_i}{V_f} \right)^{\gamma} = 1$$

Pressure change in an adiabatic process (reversible)

$$pV = nRT$$

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \qquad T_f = T_i\left(\frac{V_i}{V_f}\right)^{1/c}$$

$$\frac{p_i V_i}{p_f V_f} = \left(\frac{V_f}{V_i}\right)^{1/c}$$

$$\frac{p_i}{p_f}\left(\frac{V_i}{V_f}\right)^{\frac{1}{c}+1} = 1$$

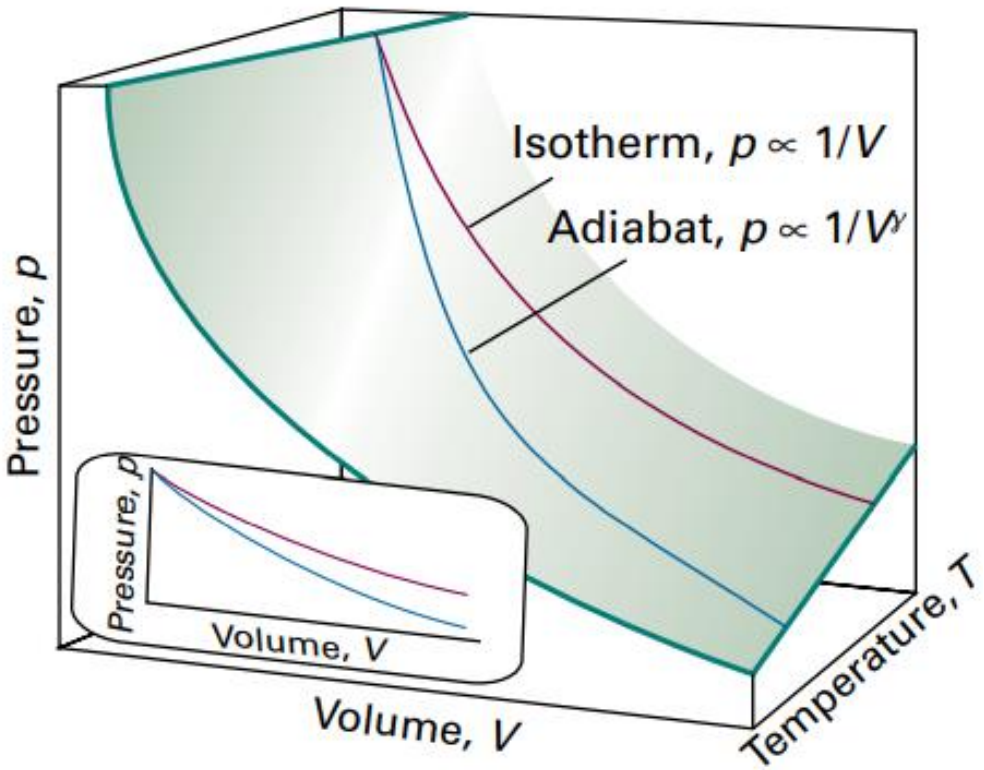
$$\frac{p_i}{p_f}\left(\frac{V_i}{V_f}\right)^{\gamma} = 1 \qquad \boxed{p_f V_f^{\gamma} = p_i V_i^{\gamma}}$$

$$\frac{1}{c} + 1 = \frac{1+c}{c} = \frac{R + C_{V,m}}{C_{V,m}} = \frac{C_{p,m}}{C_{V,m}} = \gamma$$

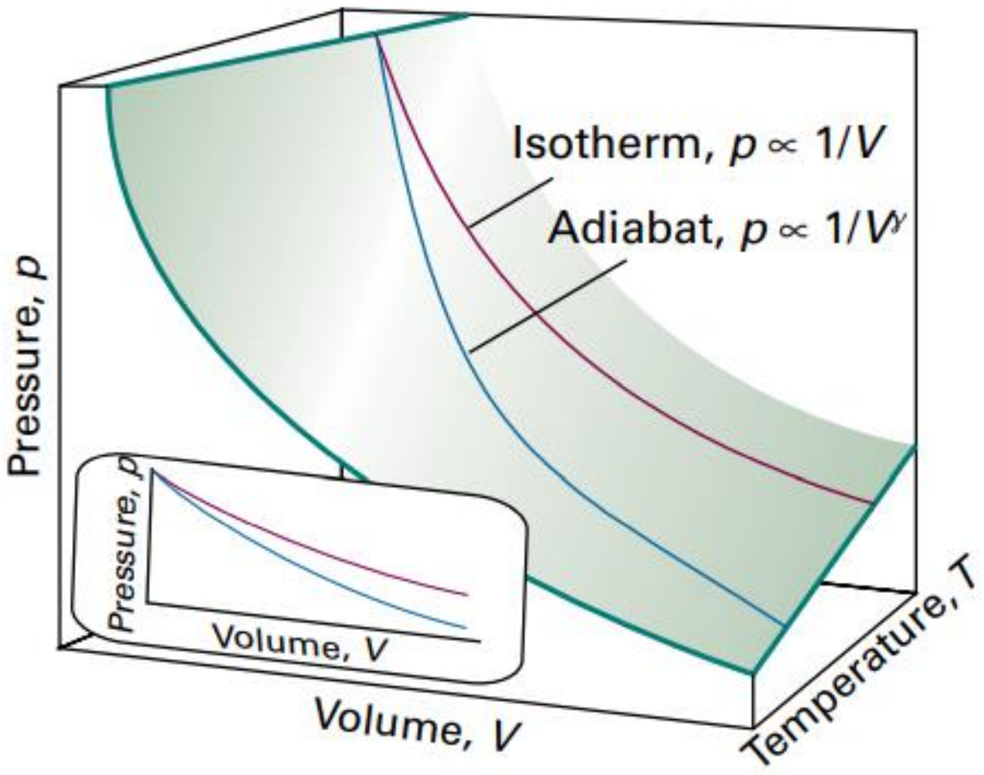
$$c = C_{V,m}/R$$

$$C_{p,m} - C_{V,m} = R$$

Adiabatic vs isothermal changes



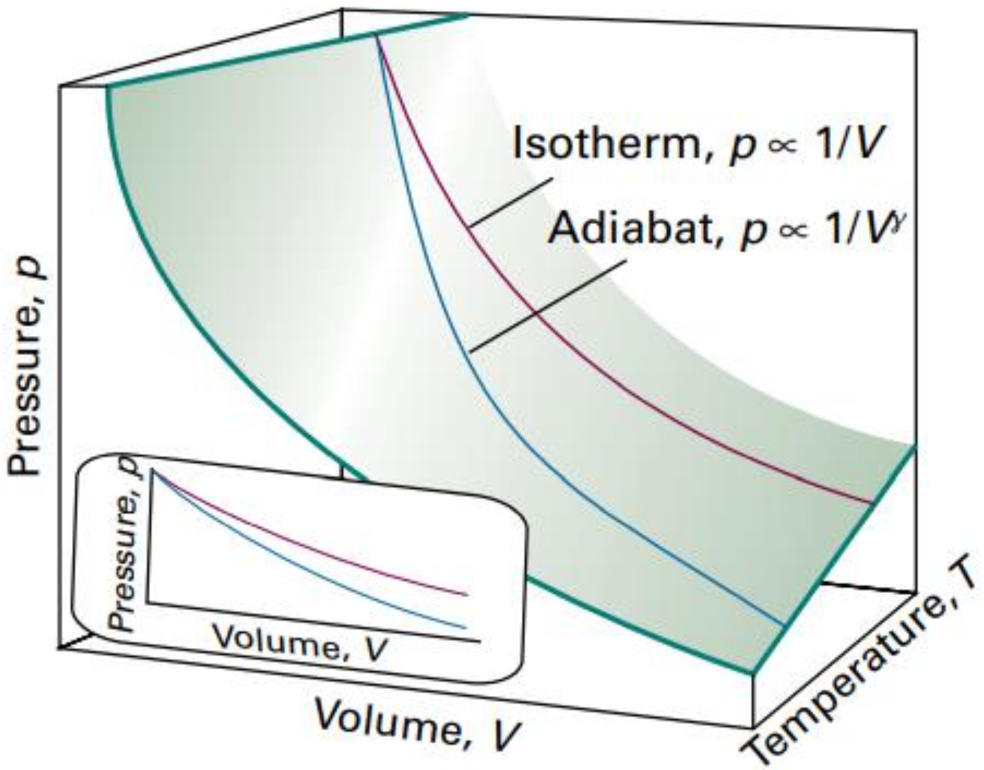
Adiabatic vs isothermal changes



pressure declines more steeply for an adiabat

$\gamma > 1$

Adiabatic vs isothermal changes



pressure declines more steeply for an adiabat

$$\gamma > 1$$

The steeper pressure drop during an adiabatic expansion compared to an isothermal expansion is primarily due to the temperature drop that occurs in the adiabatic process.

Value of γ

For a monatomic perfect gas,

$$C_{V,m} = \tfrac{3}{2}R$$

value comes directly from the kinetic theory of gases and the equipartition theorem in statistical mechanics

Value of γ

For a monatomic perfect gas,

$$C_{V,\mathrm{m}} = \tfrac{3}{2}R$$

$$C_{p,\mathrm{m}} = \tfrac{5}{2}R \text{ (from } C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R\text{)}$$

Value of γ

For a monatomic perfect gas,

$$C_{V,\mathrm{m}} = \tfrac{3}{2}R$$

$$C_{p,\mathrm{m}} = \tfrac{5}{2}R \ (\text{from } C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R)$$

$$\gamma = \tfrac{5}{3}$$

Value of γ

For a monatomic perfect gas,

$$C_{V,\mathrm{m}} = \tfrac{3}{2}R$$

$$C_{p,\mathrm{m}} = \tfrac{5}{2}R \text{ (from } C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R)$$

$$\gamma = \tfrac{5}{3}$$

For a gas of nonlinear polyatomic molecules

$$C_{V,\mathrm{m}} = 3R$$

$$C_{p,\mathrm{m}} = 4R$$

$$\gamma = \tfrac{4}{3}$$

CHEM3520 - Spring 2023

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 16: Molecules in motion

Focus 17: Chemical kinetics

Focus 18: Reaction dynamics

Focus 19: Processes at solid surfaces