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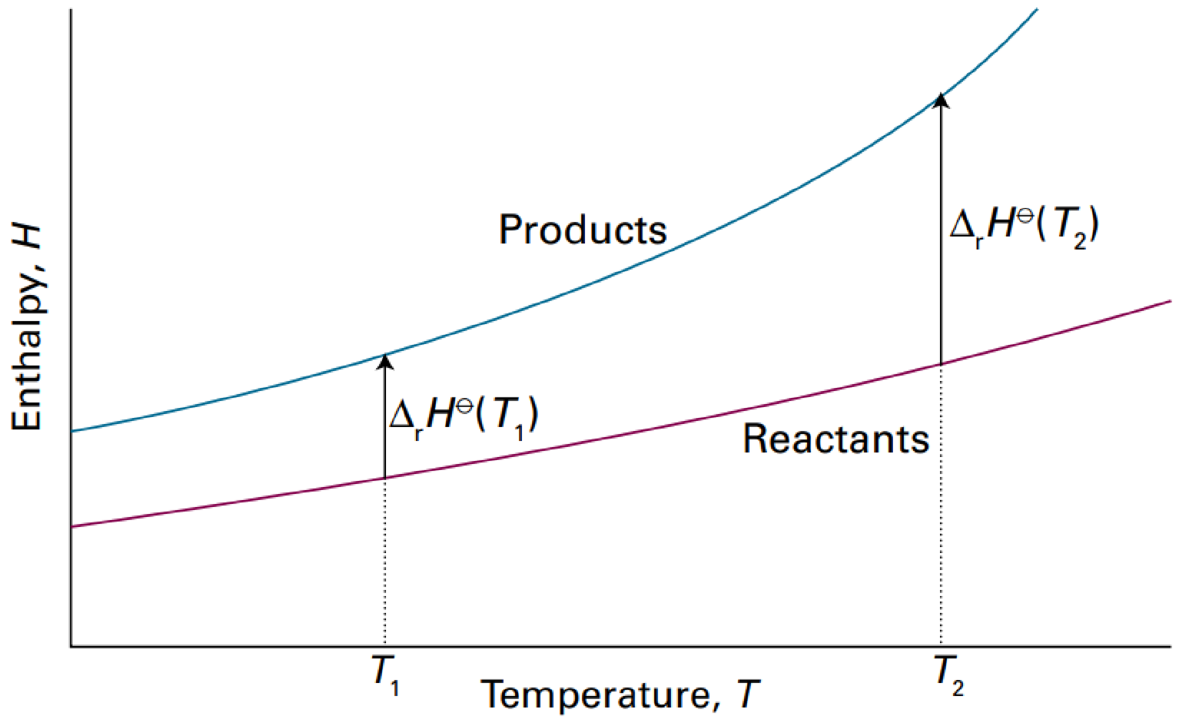
If no phase transition takes place

# Temperature dependence of reaction enthalpies

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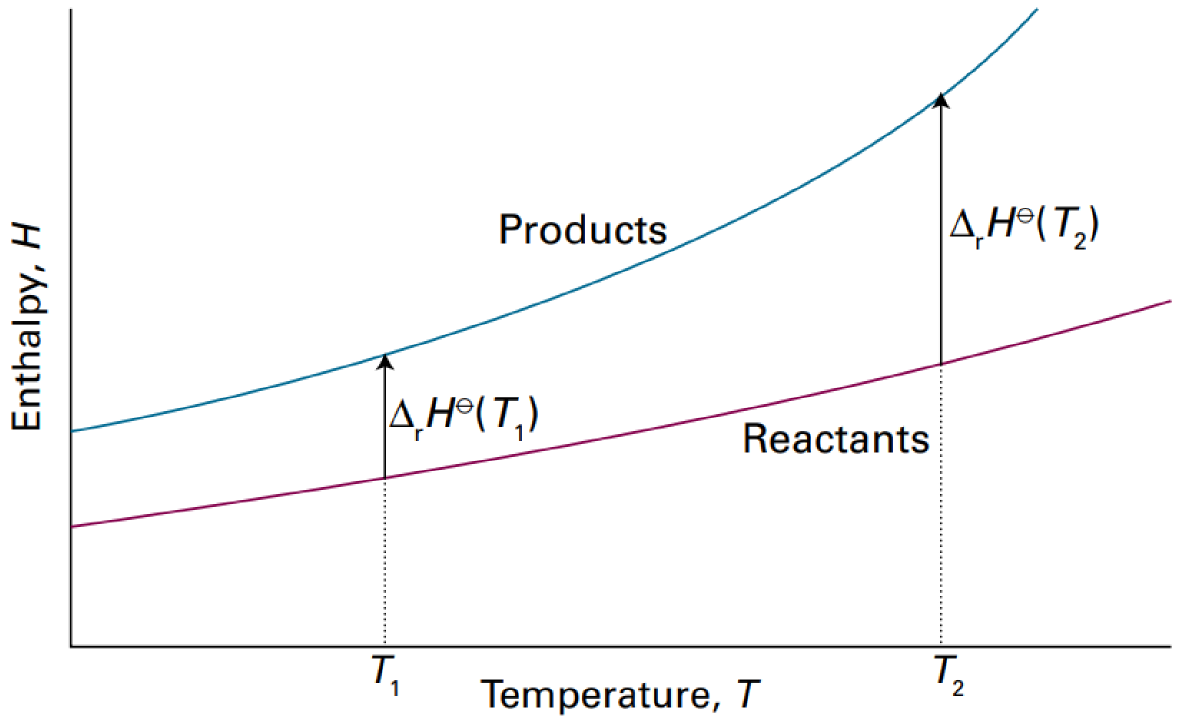


Kirchhoff's law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus \, dT$$

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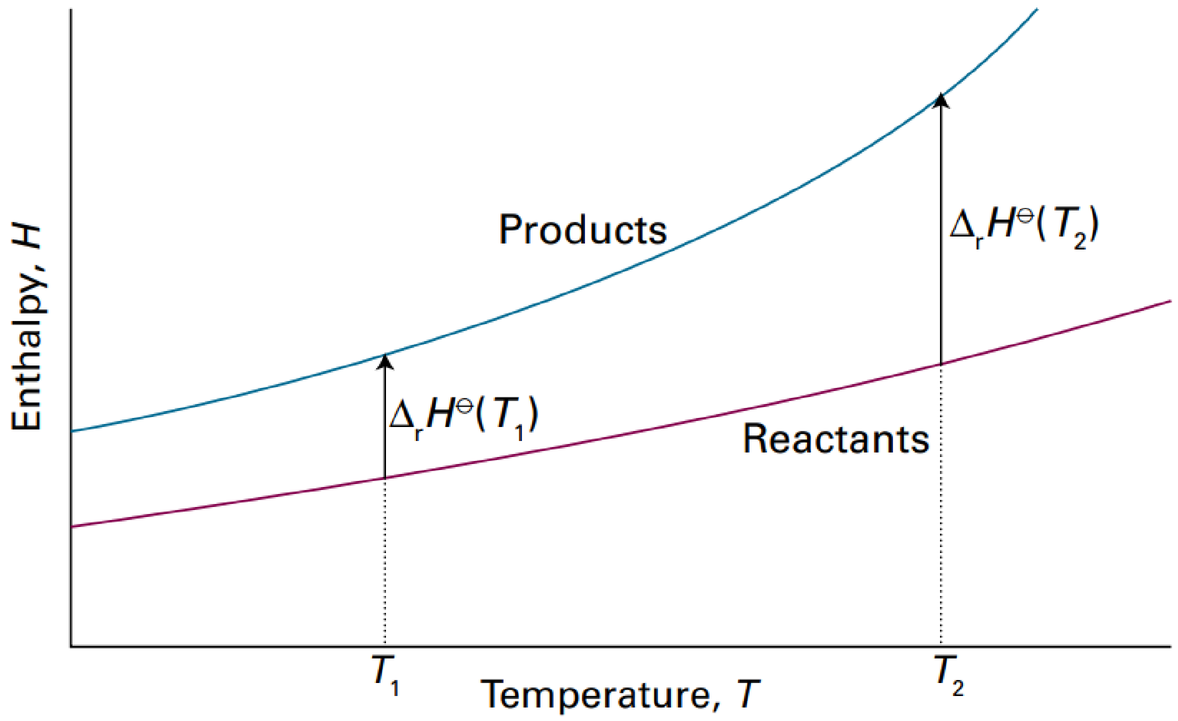


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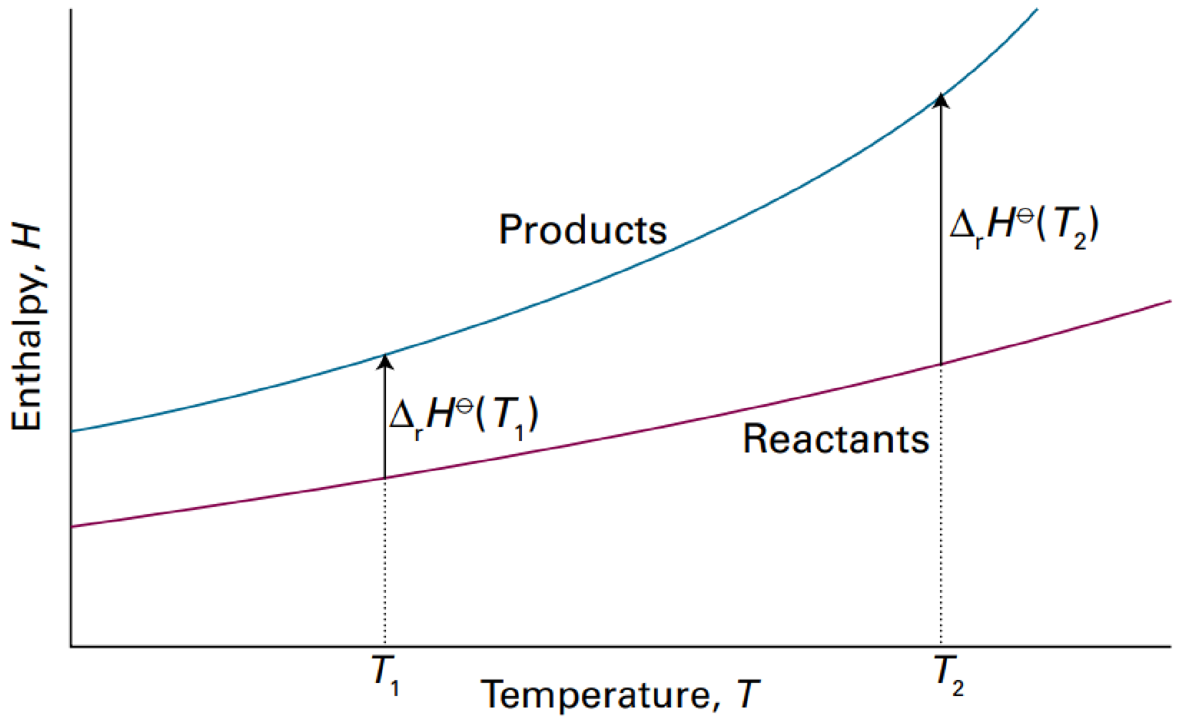


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Integrated form of Kirchhoff's law

The difference in heat capacities varies less significantly

$$dH = C_p dT$$

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If no phase transition takes place

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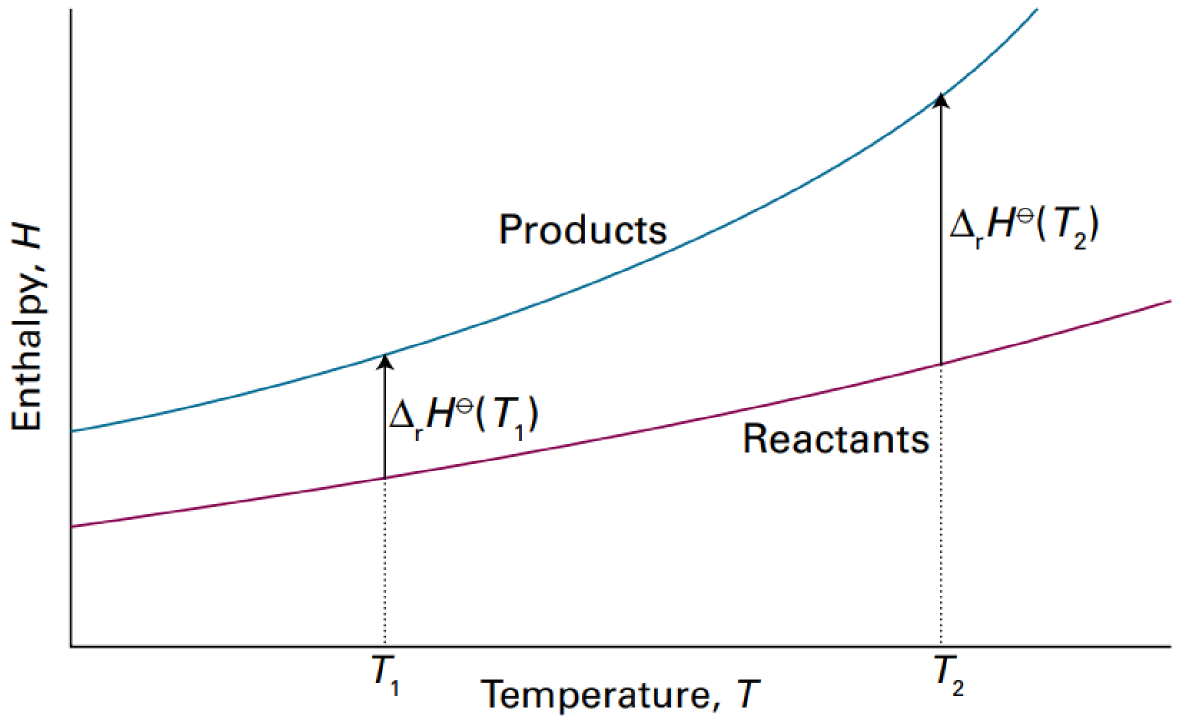


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If no phase transition takes place

## Calculation

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g)$$

The standard enthalpy of formation of $H_2O(g)$ at 298 K is $-241.82\ \mathrm{kJ\,mol^{-1}}$. Estimate its value at 100 °C given the following values of the molar heat capacities at constant pressure: $H_2O(g)$: $33.58\ \mathrm{J\,K^{-1}\,mol^{-1}}$; $H_2(g)$: $28.84\ \mathrm{J\,K^{-1}\,mol^{-1}}$; $O_2(g)$: $29.37\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Assume that the heat capacities are independent of temperature.

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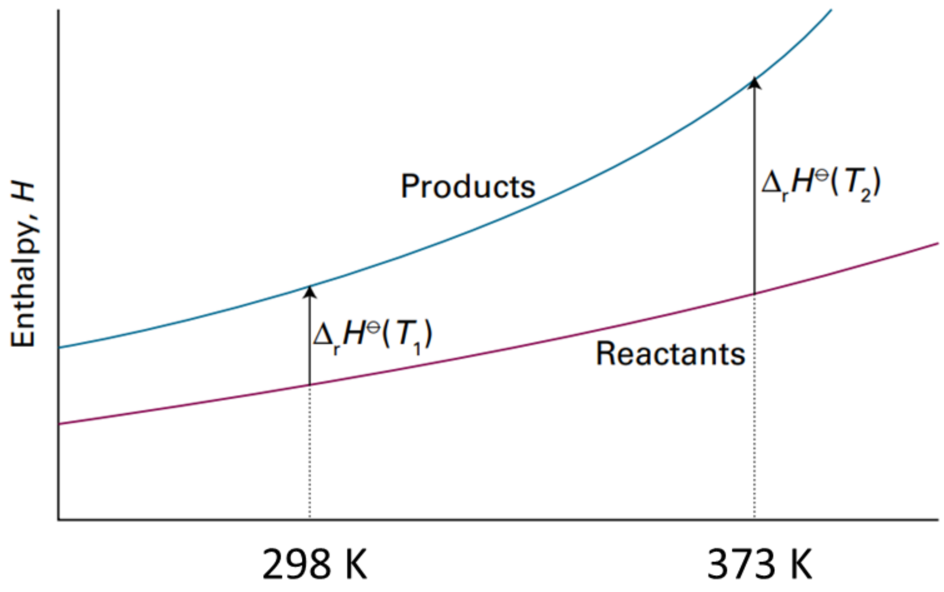

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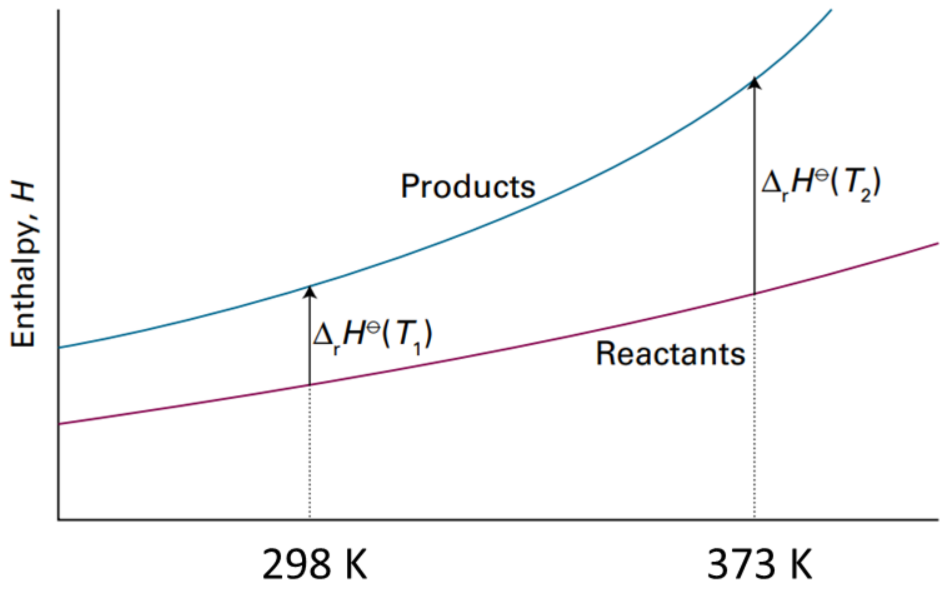

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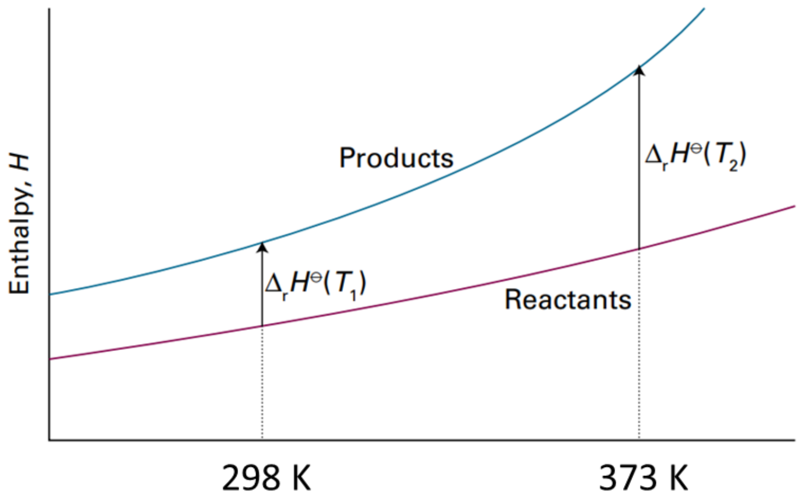

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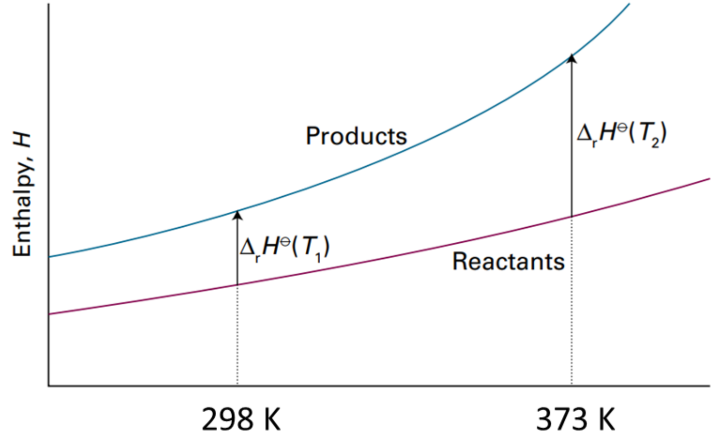


Kirchhoff's law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \underbrace{\Delta_r C_p^\ominus}(T_2 - T_1)$$

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$$\Delta_r C_p^\ominus = C_{p,m}^\ominus(H_2O,g) - \{C_{p,m}^\ominus(H_2,g) + \tfrac{1}{2}C_{p,m}^\ominus(O_2,g)\}$$
$$= -9.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

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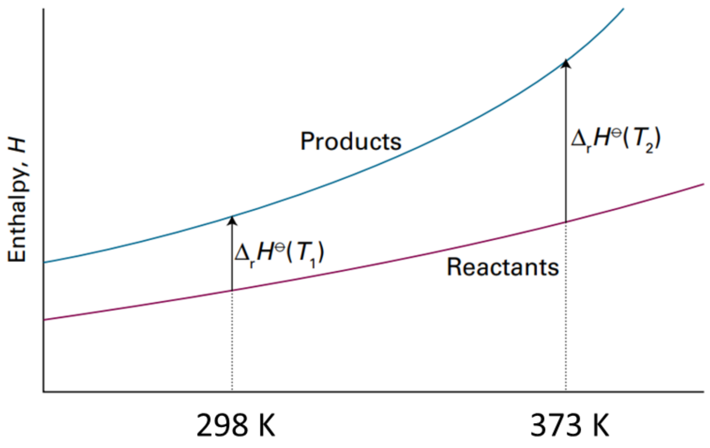


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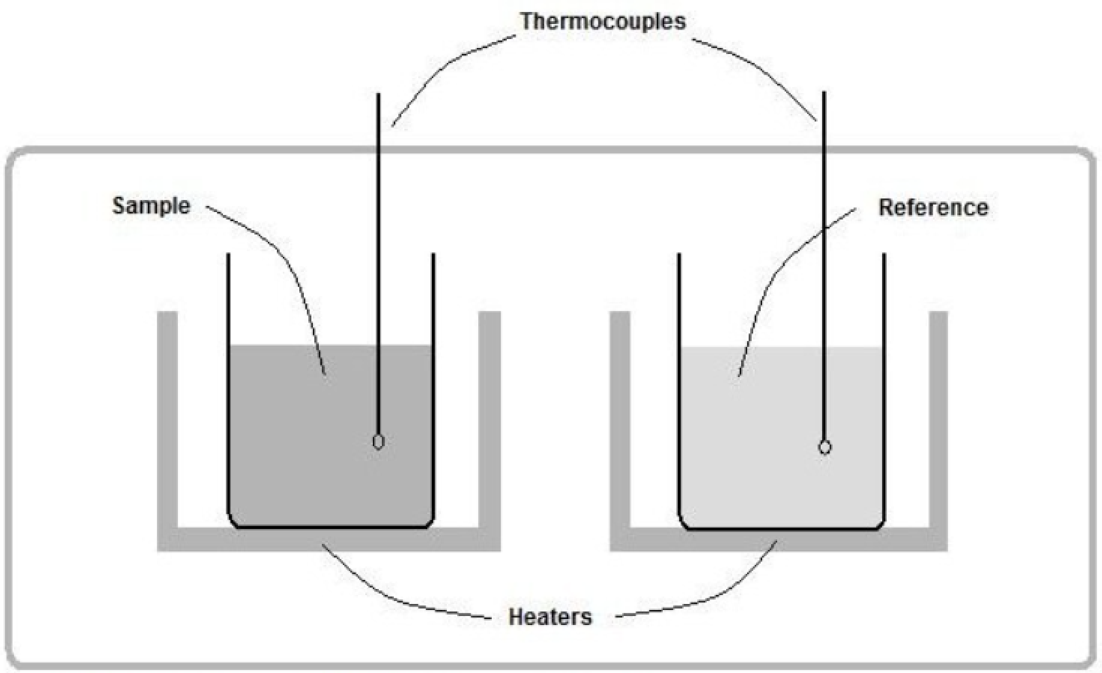
$$\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \Delta_r C_p^{\ominus}(T_2 - T_1)$$

$\Delta_r H^{\ominus}(T_1)$: −241.82 kJ mol$^{-1}$

$$\Delta_r C_p^{\ominus} = C_{p,m}^{\ominus}(H_2O,g) - \{C_{p,m}^{\ominus}(H_2,g) + \tfrac{1}{2}C_{p,m}^{\ominus}(O_2,g)\}$$
$$= -9.94\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\Delta_r H^{\ominus}(373\ \mathrm{K}) = -241.82\ \mathrm{kJ\,mol^{-1}} + (75\ \mathrm{K}) \times (-9.94\ \mathrm{J\,K^{-1}\,mol^{-1}}) = -242.6\ \mathrm{kJ\,mol^{-1}}$$

# Differential Scanning Calorimetry




- Sample and reference (solvent) reside in separate chambers
- Separate sources heat the chambers in a way that their temperatures are always equal
- The heating rates, which were used to maintain equivalent temperatures, are logged
- Any difference between the two can be attributed to the presence of the substance of interest

# Focus 2: The First Law

**Internal Energy**

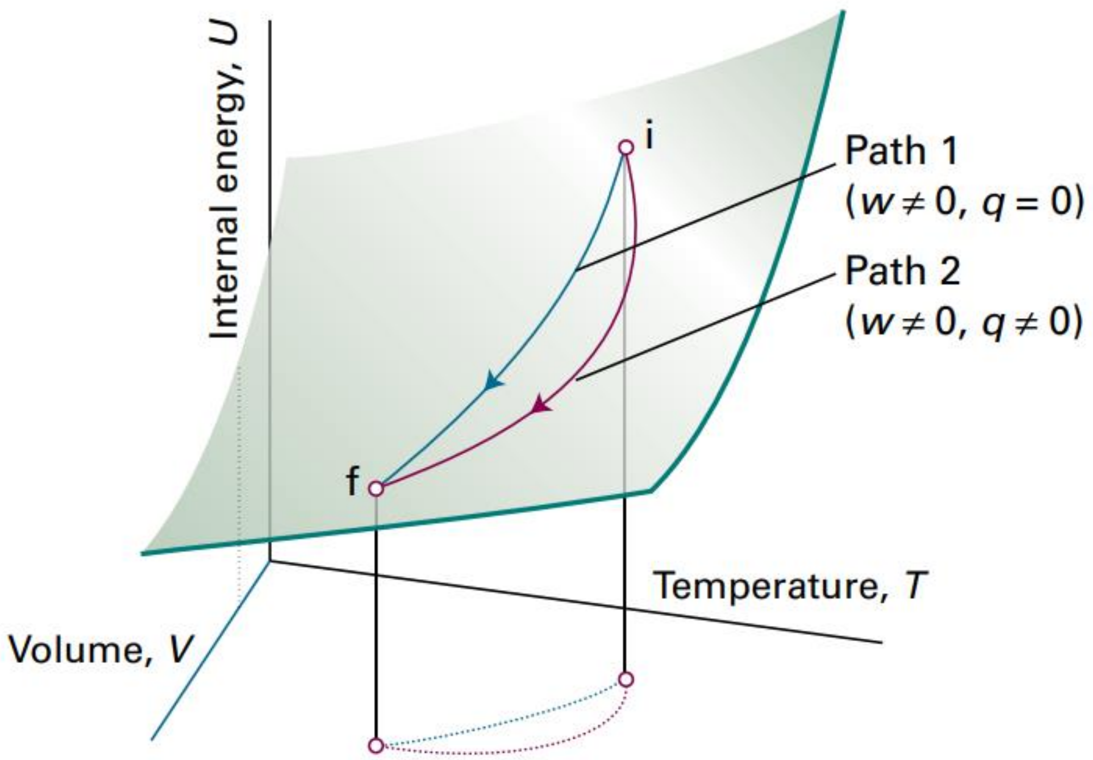
**Enthalpy**

**Thermochemistry**

State functions

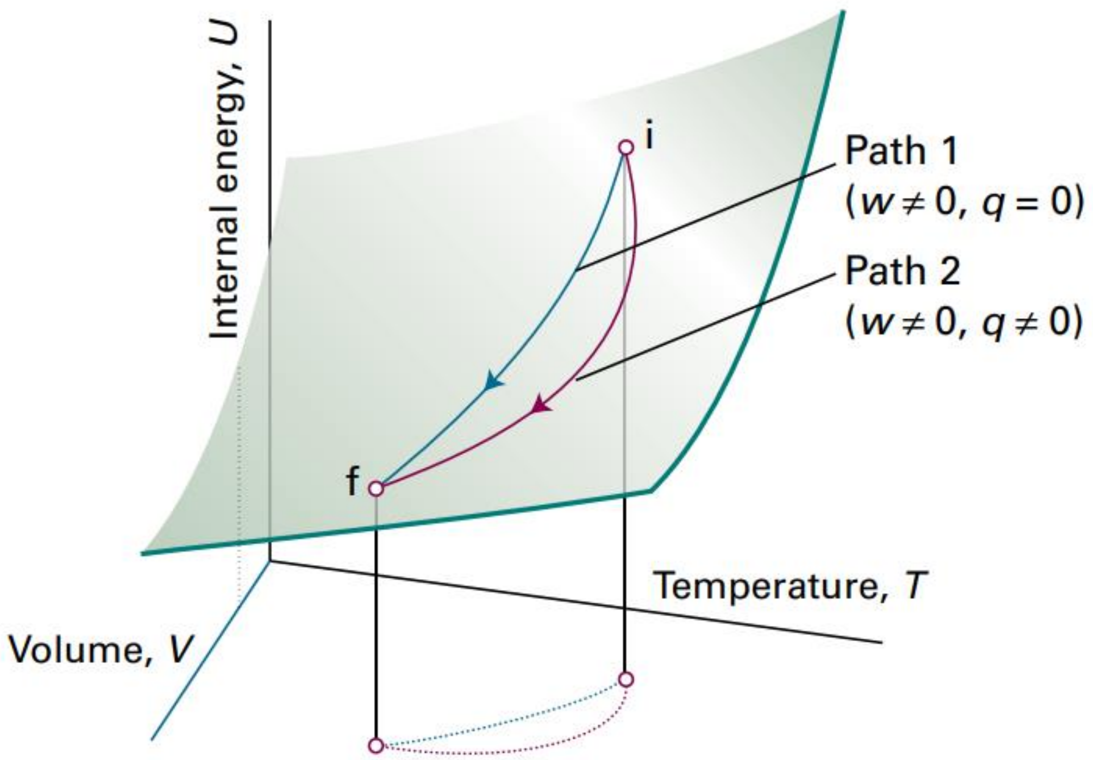
Adiabatic changes

# Exact and inexact differentials



# Exact and inexact differentials

$$\Delta U = \int_i^f dU$$

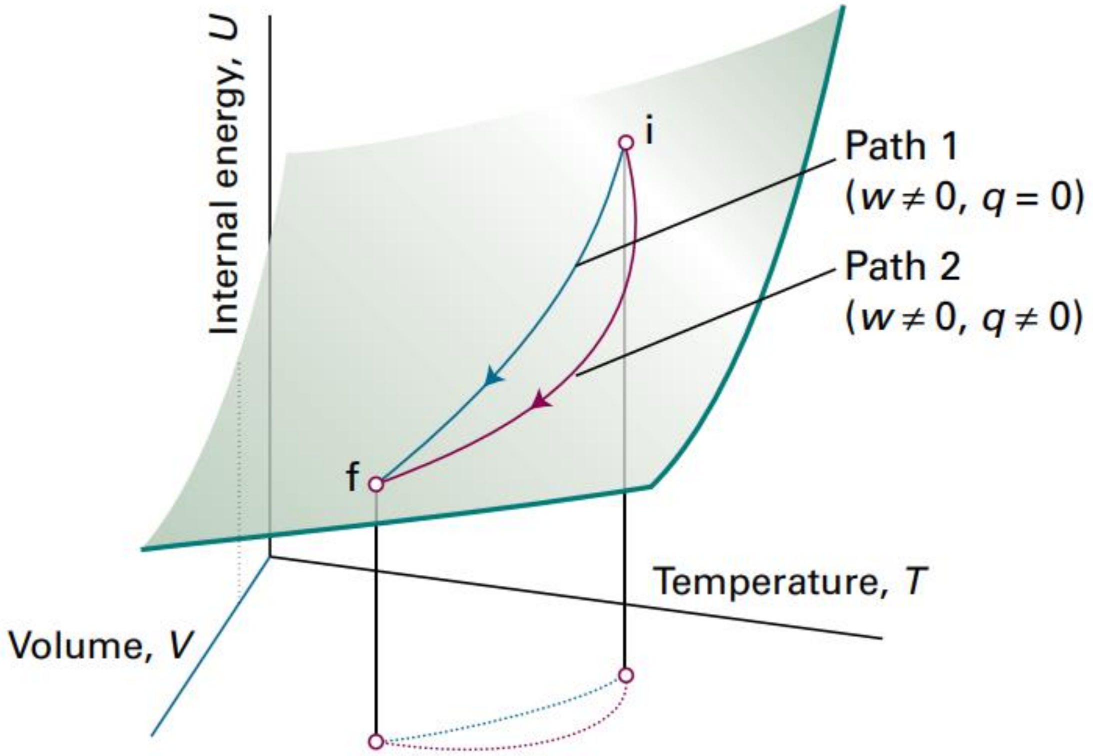


# Exact and inexact differentials

$$\Delta U = \int_i^f dU$$

**exact differential**

A differential dX is called exact if it represents the differential of a state function



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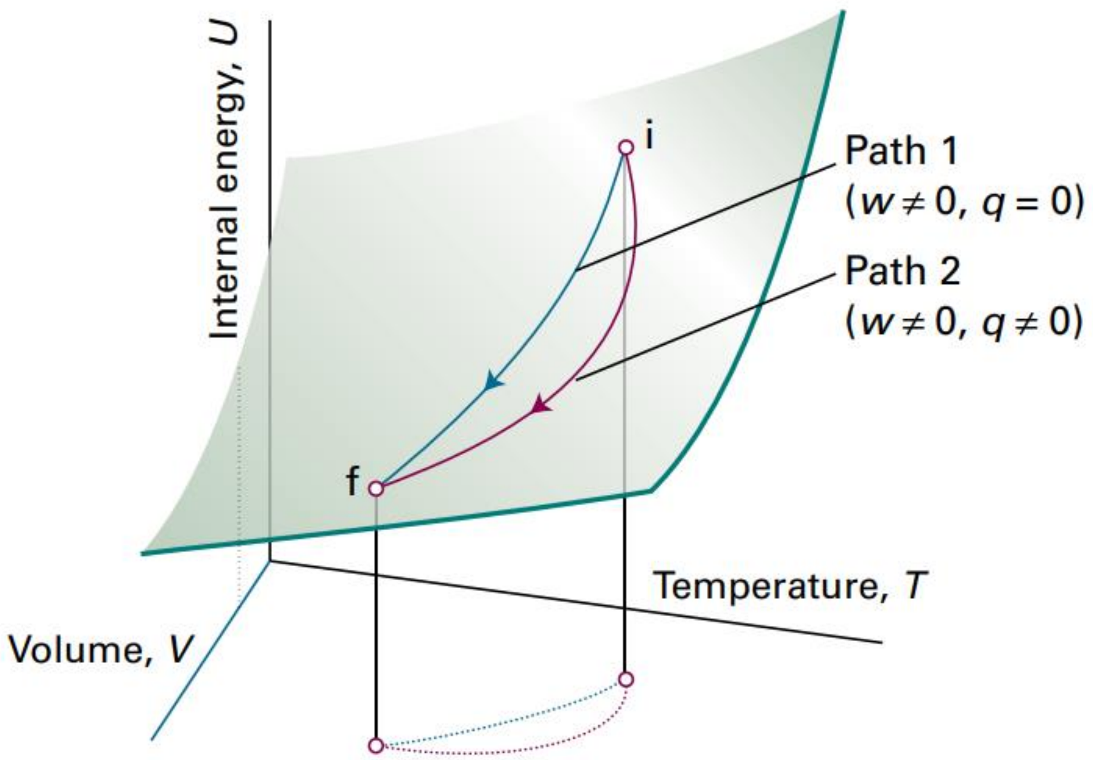
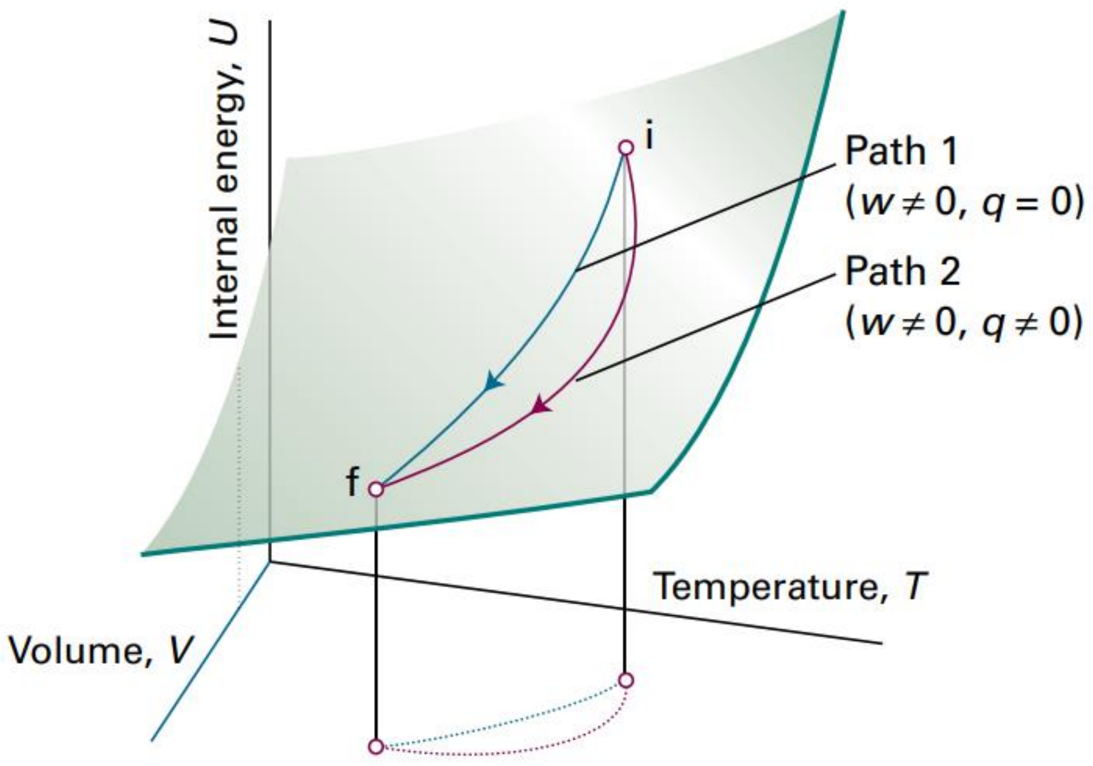



$$q = \int_{i,\text{path}}^{f} dq$$

# Exact and inexact differentials




$$\Delta U = \int_{i}^{f} dU$$

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$$q = \int_{i,path}^{f} dq$$

**inexact differential**

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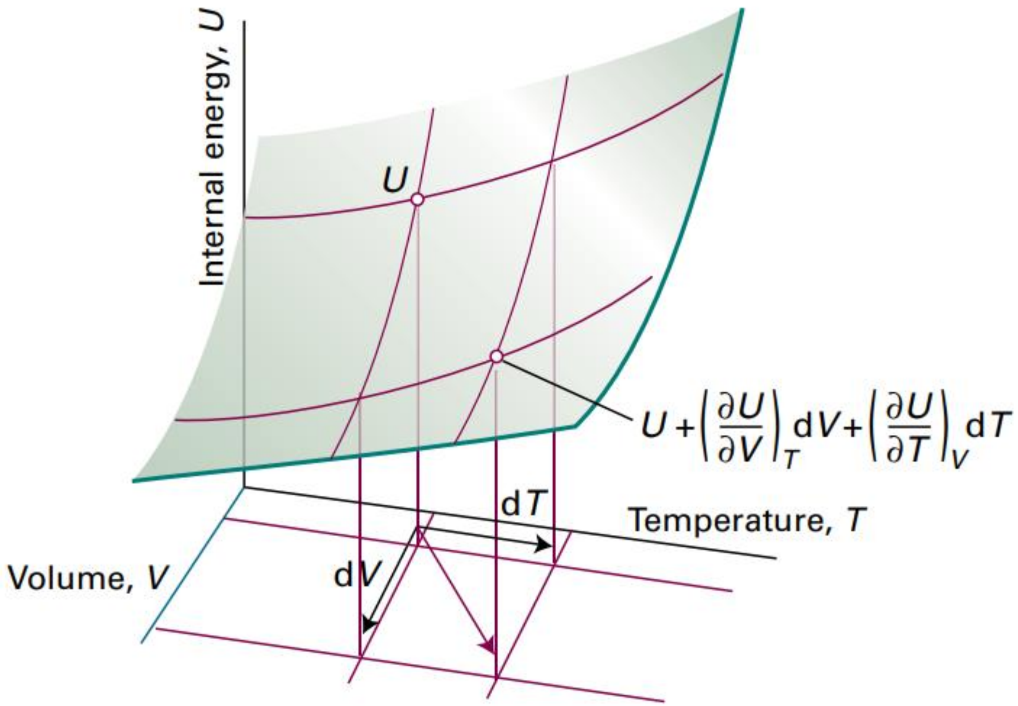
# Changes in internal energy



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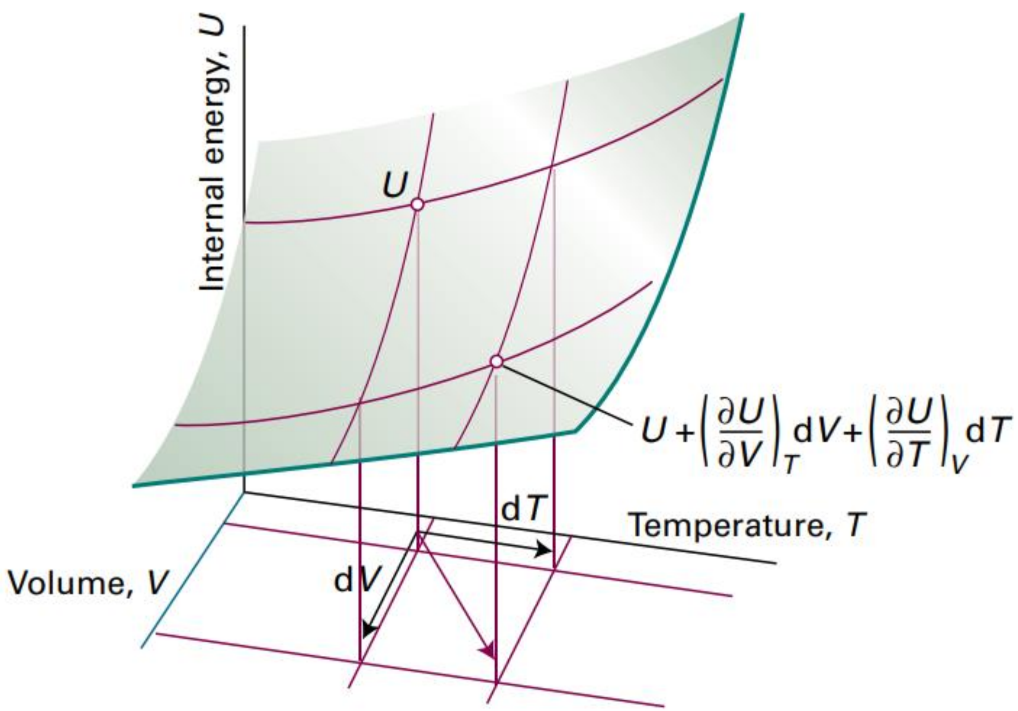
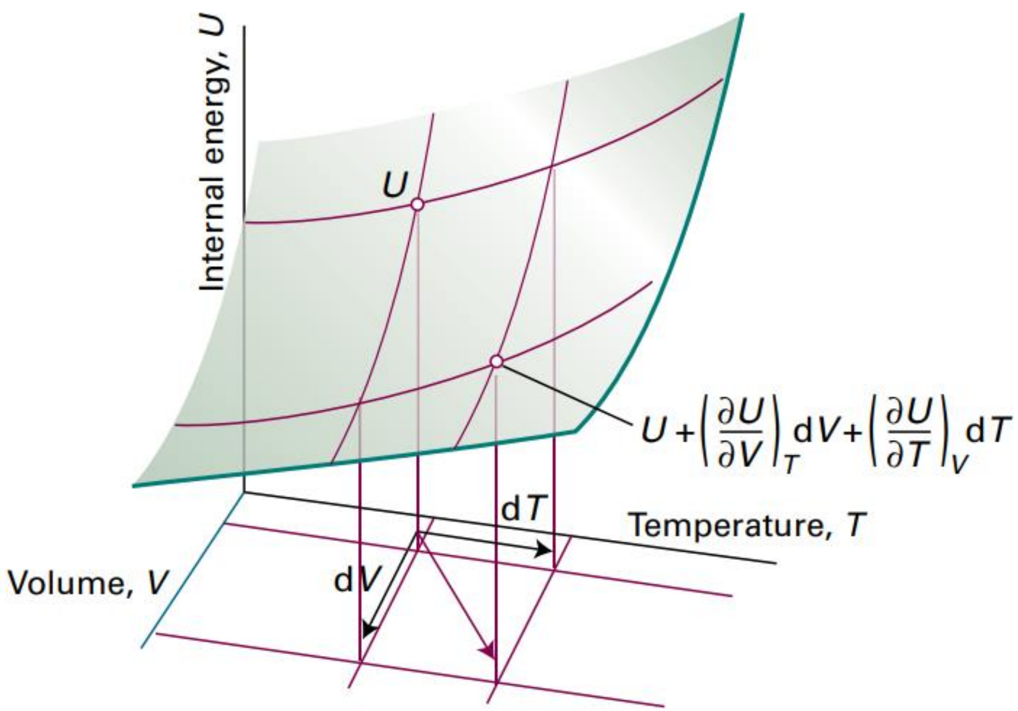



If a function U(V,T) depends on two independent variables v and T:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

# Changes in internal energy




$$C_V$$

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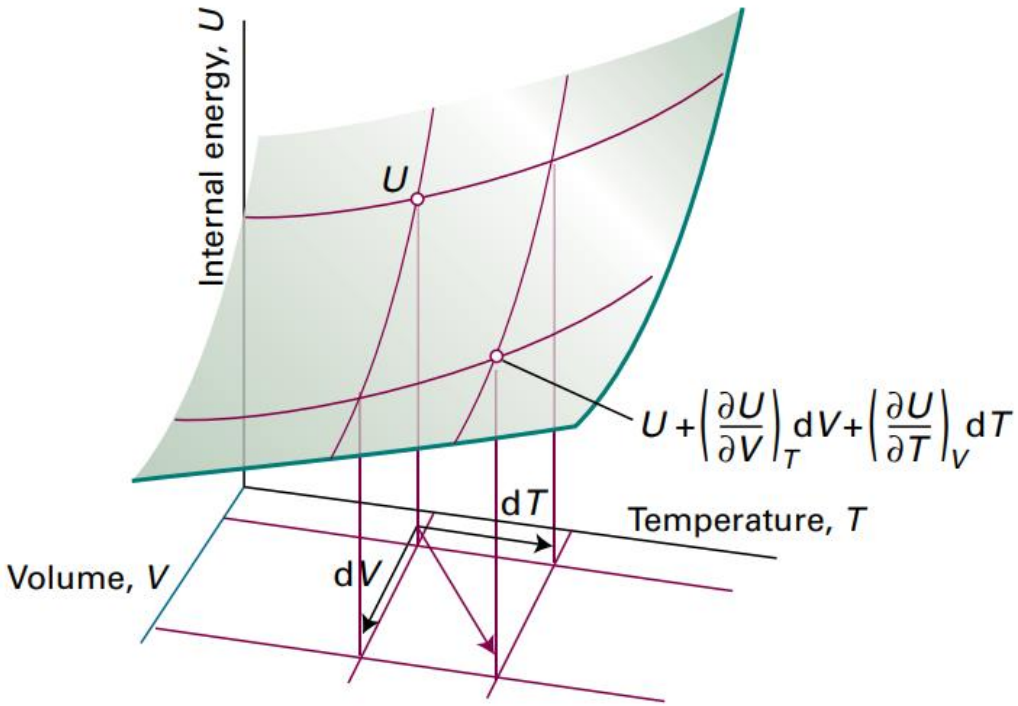


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**internal pressure**

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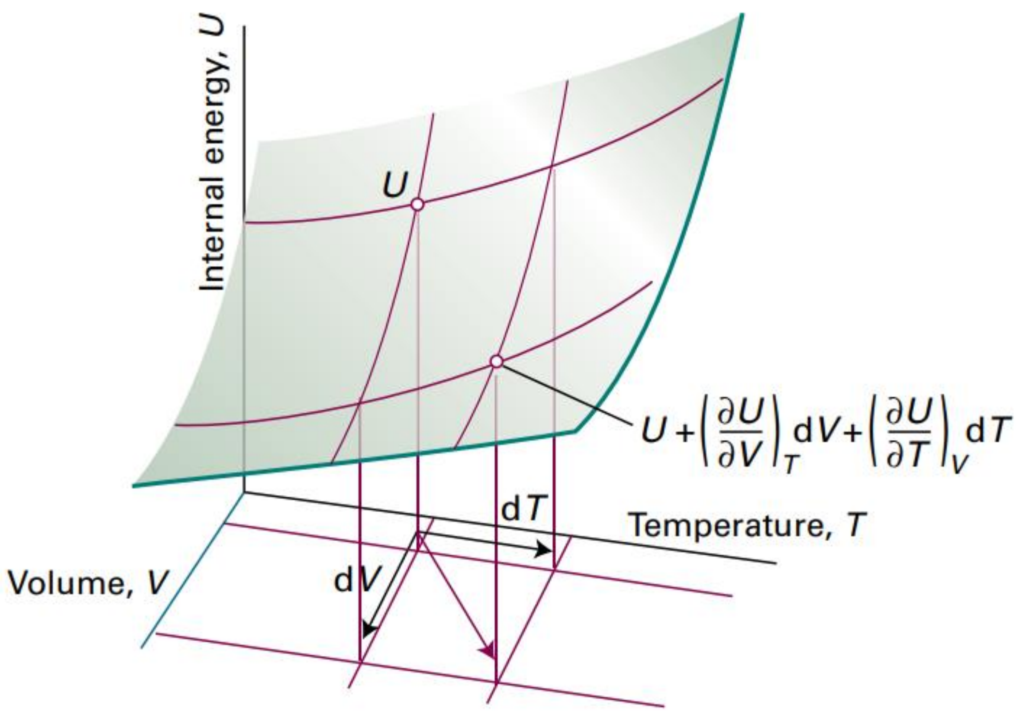


$C_V$

$$dU=\left(\frac{\partial U}{\partial V}\right)_T dV+\left(\frac{\partial U}{\partial T}\right)_V dT$$

**internal pressure**

$$dU=\pi_T dV+C_V dT$$

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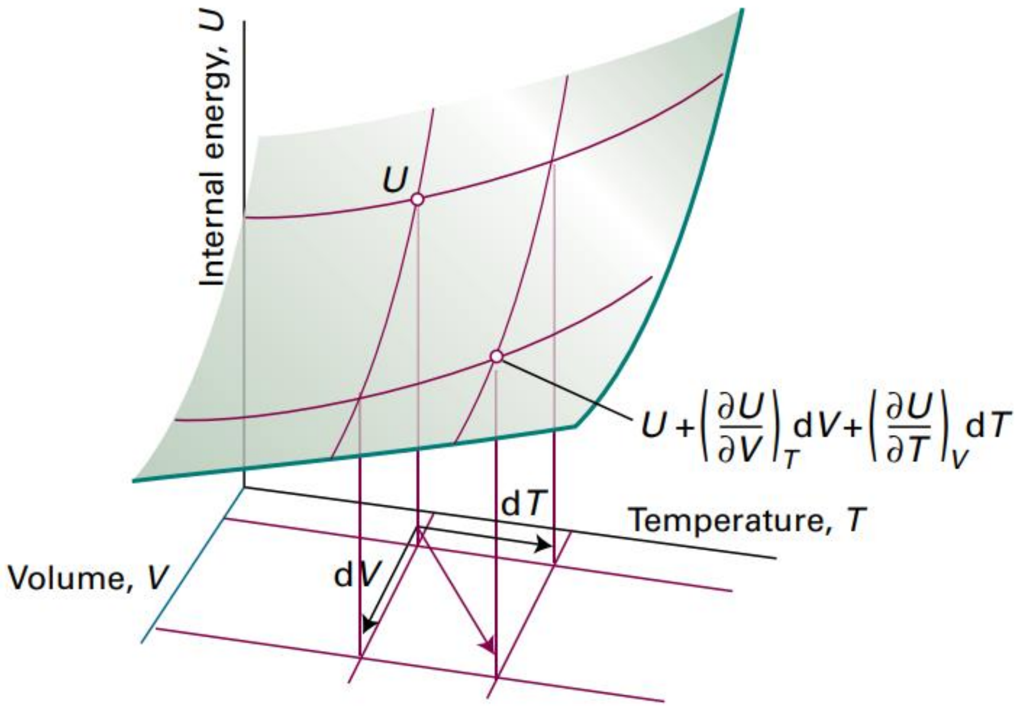


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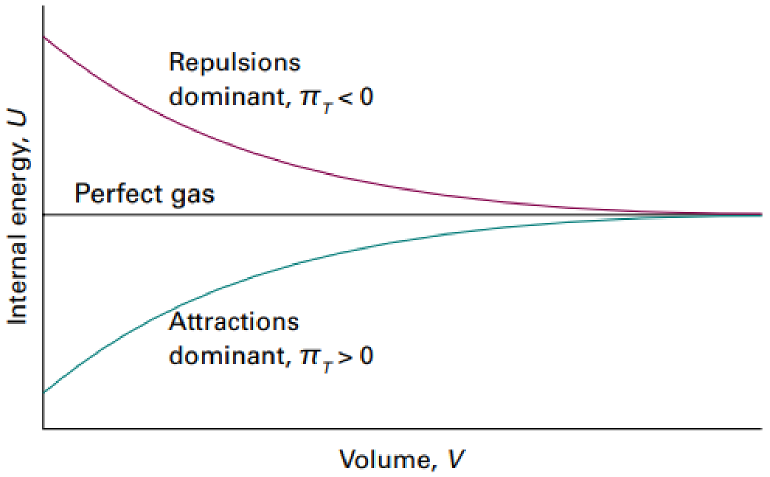
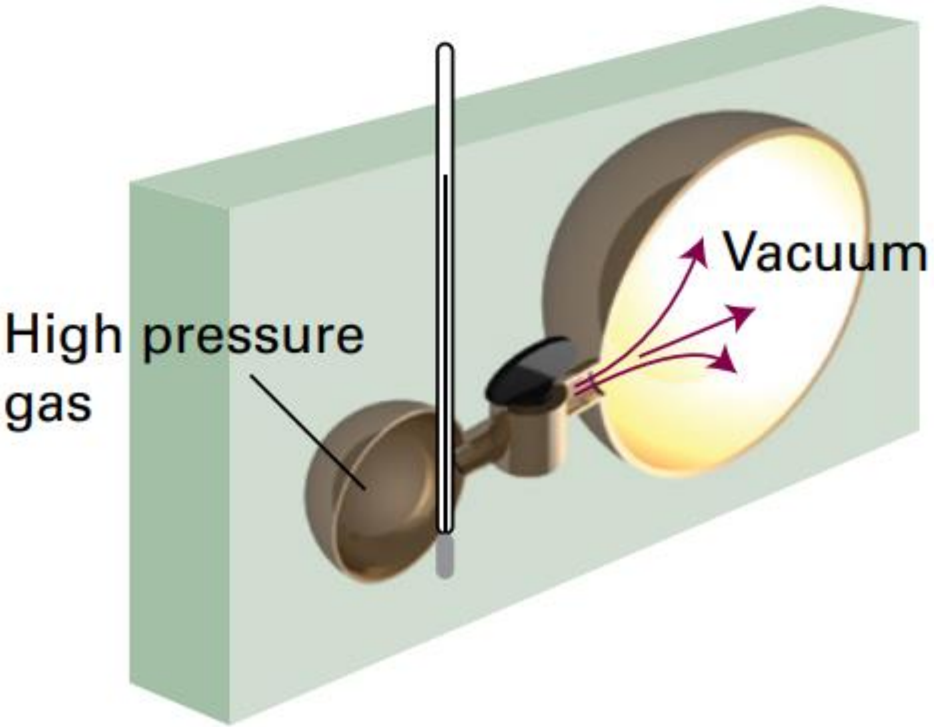



$\pi_T = 0$ for perfect gases

# Measuring $\pi_T$

isothermal




James Prescott Joule (1818 – 1889) was an English physicist

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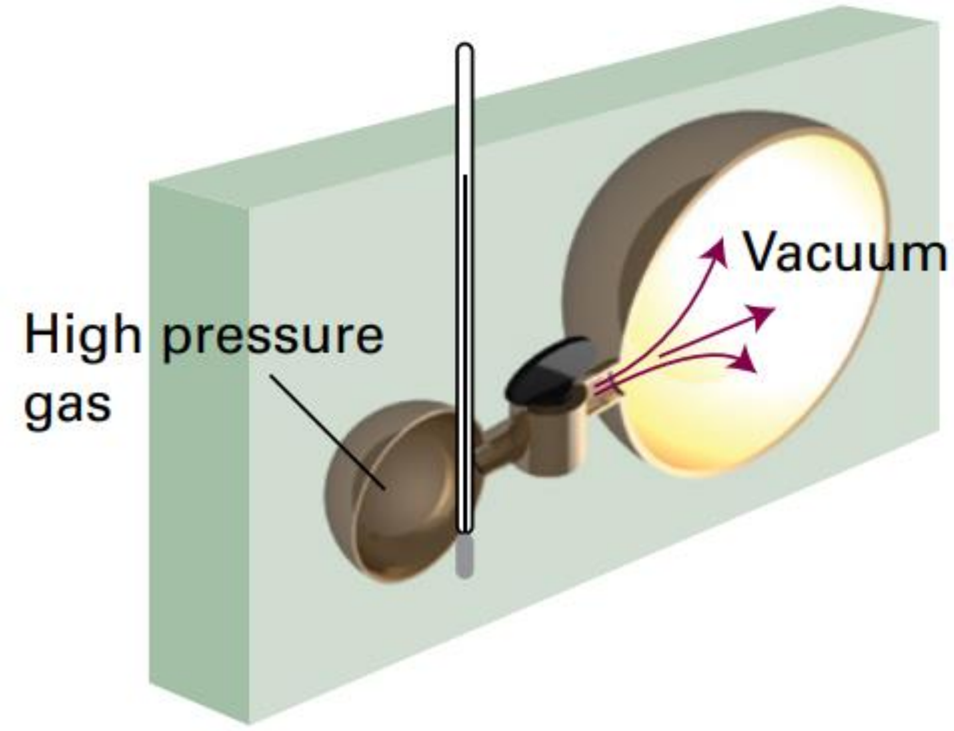


$w = 0$

$q = 0$

$\Delta U = 0$

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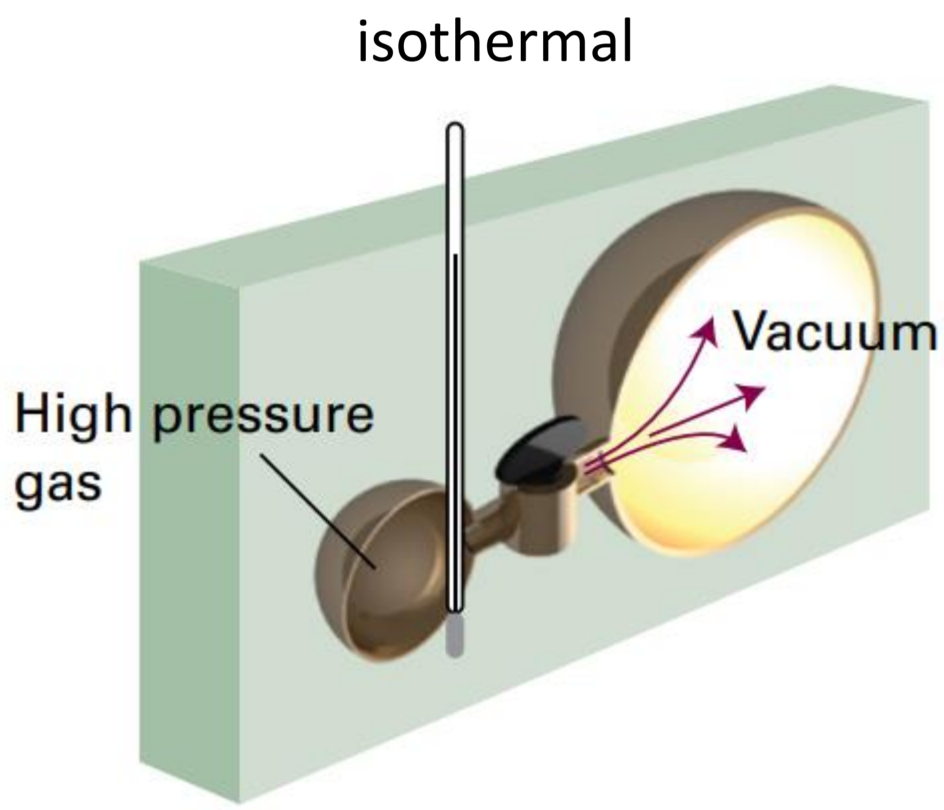
# Measuring $\pi_T$

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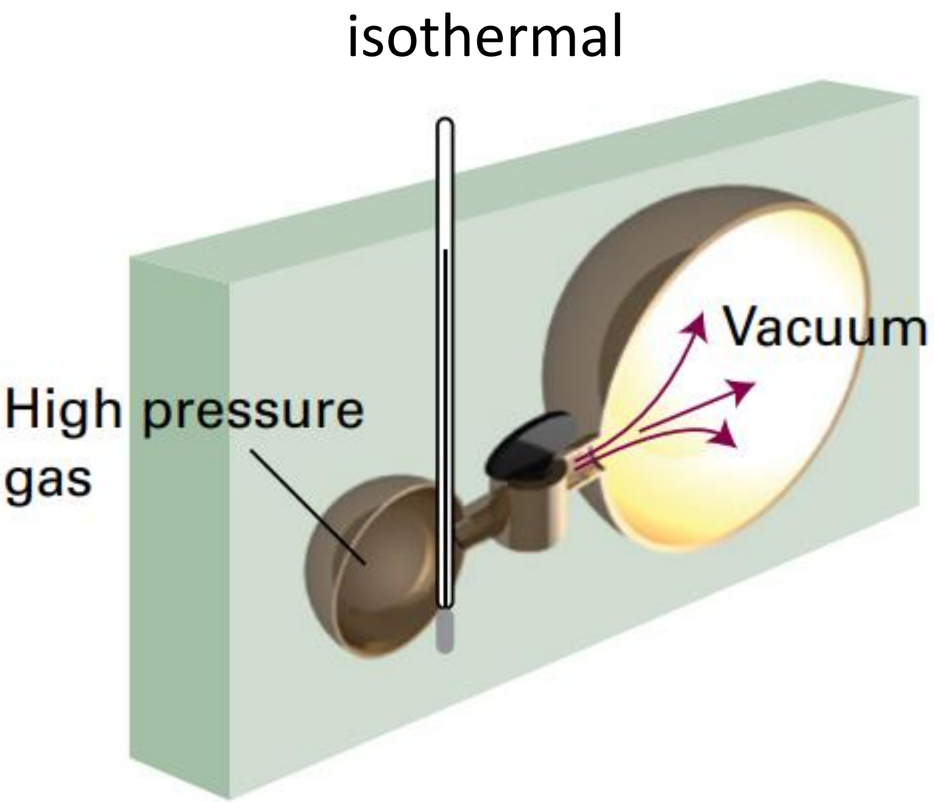


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Joule concluded that U does not change when a gas expands isothermally and therefore that $\pi_T = 0$.

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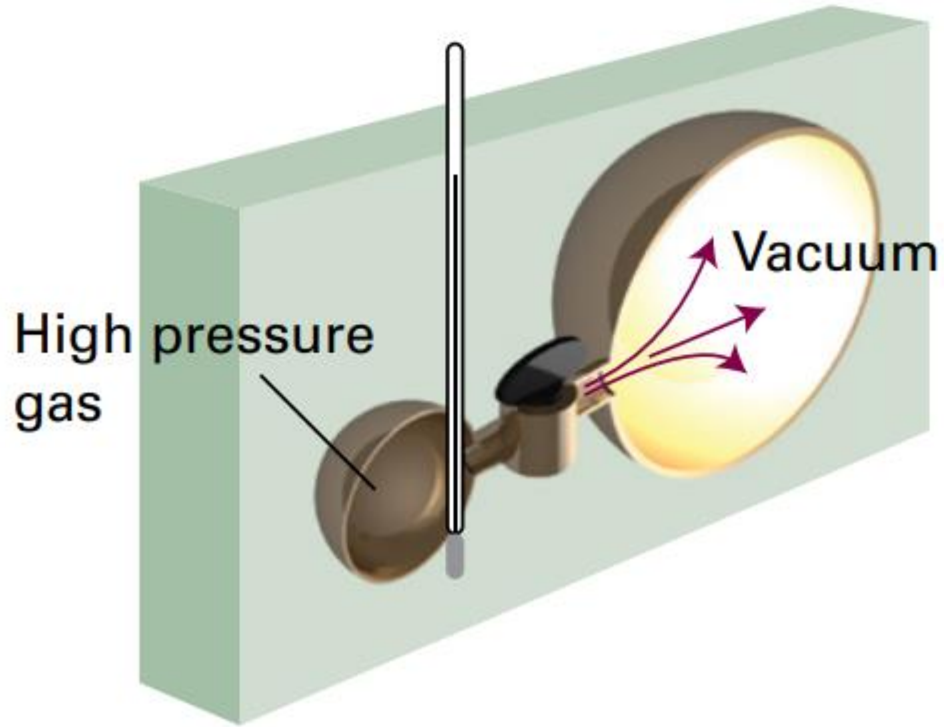


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Joule extracted a limited property of gas, a characteristic of a perfect gas, without noticing the small deviations in real gases.

Joule concluded that U does not change when a gas expands isothermally and therefore that $\pi_T = 0$.

# Expansion and isothermal coefficients

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

expansion coefficient

# Expansion and isothermal coefficients

| | $\alpha/(10^{-4}\ \mathrm{K}^{-1})$ | $\kappa_T/(10^{-6}\ \mathrm{bar}^{-1})$ |
|---|---|---|
| *Liquids:* | | |
| Benzene | 12.4 | 90.9 |
| Water | 2.1 | 49.0 |
| *Solids:* | | |
| Diamond | 0.030 | 0.185 |
| Lead | 0.861 | 2.18 |

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For a perfect gas;

$$\kappa_T = 1/p$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

expansion coefficient

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

isothermal compressibility