Focus 3: The Second and Third Laws

- **Entropy**
- Entropy changes in processes
- Entropy measurement
- Gibbs free energy
- Combining 1st and 2nd law

Thermodynamic definition of S

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

$J\,K^{-1}$

extensive property

Calculate the entropy change of a sample of perfect gas when it expands isothermally from a volume V_i to a volume V_f

$$\Delta U = q + w$$

$$q = -w = nRT\ln(V_f/V_i)$$

$$\Delta S = \frac{1}{T}\int_i^f dq_{rev} = \frac{q_{rev}}{T}$$

$$\Delta S = nR\ln\frac{V_f}{V_i}$$

$$\Delta S_m = R\ln\frac{V_f}{V_i}$$

Reversible Isothermal Expansion

$$\Delta S = nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

Entropy change for the isothermal expansion of a perfect gas

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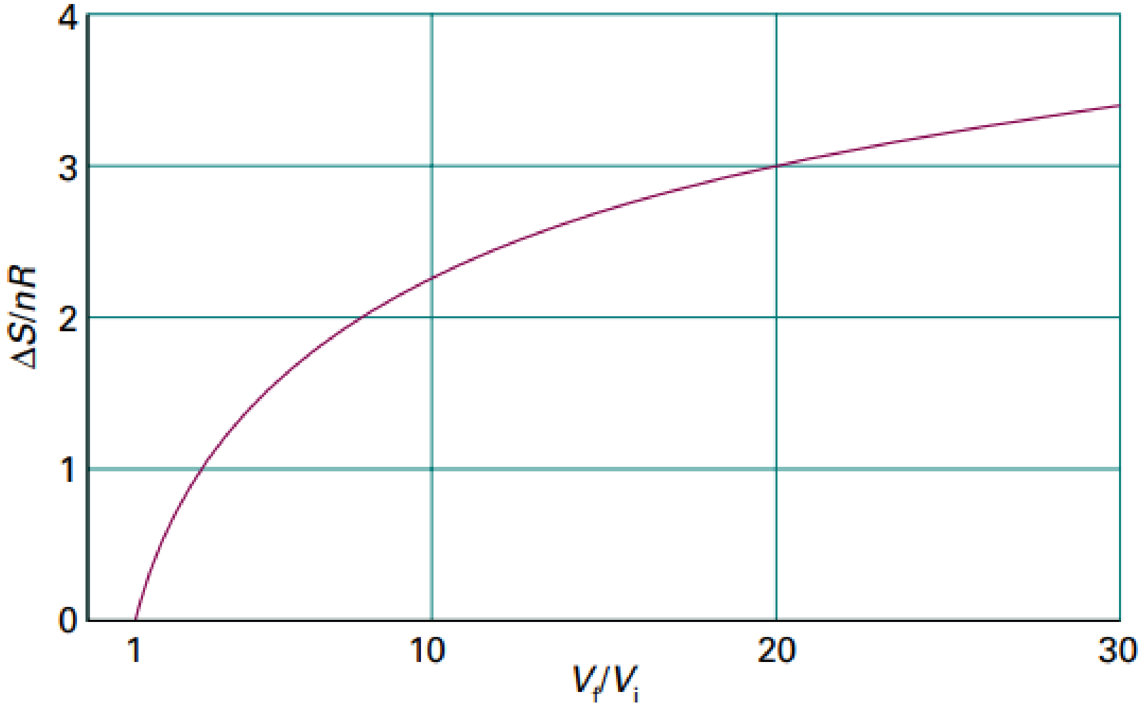

logarithmic dependence of entropy on volume

Expansion

The total change in entropy, depends on how the expansion takes place

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Even if the gas expands into a larger volume within an isolated container, the external surroundings do not experience a change in the thermodynamic state.

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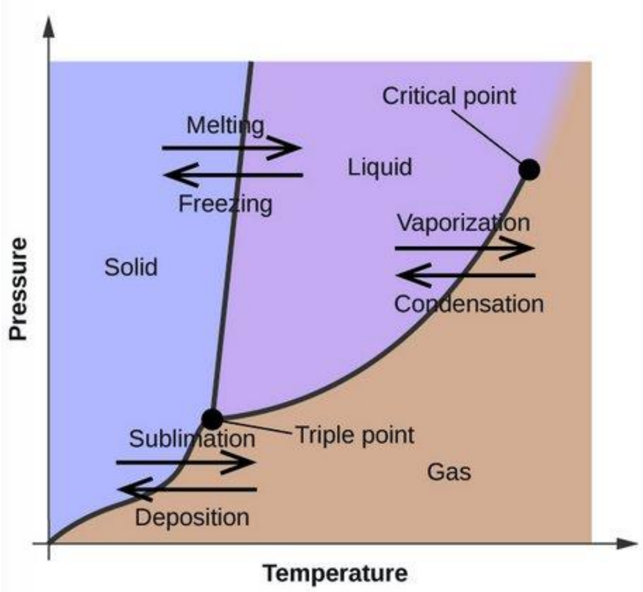
Irreversible process!

Phase transitions

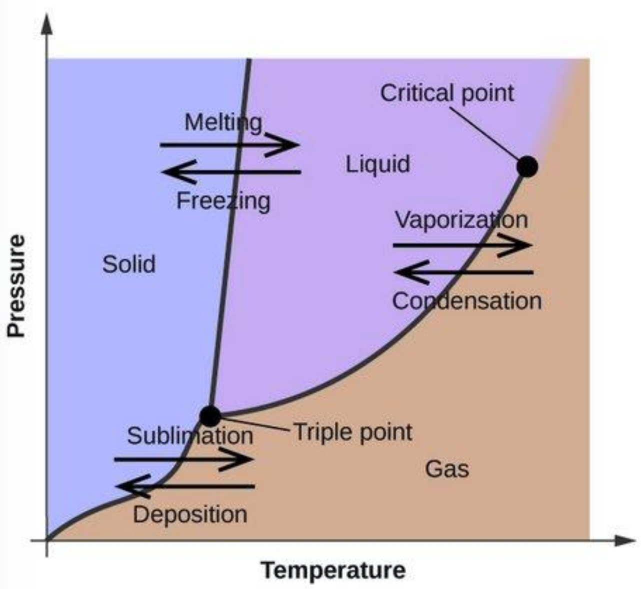


Phase transitions

- When a system undergoes a phase change at the transition temperature, any heat transfer (q) is reversible.

- This is because adding heat causes some of the substance to transition into the next phase (e.g., from solid to liquid) without changing temperature.

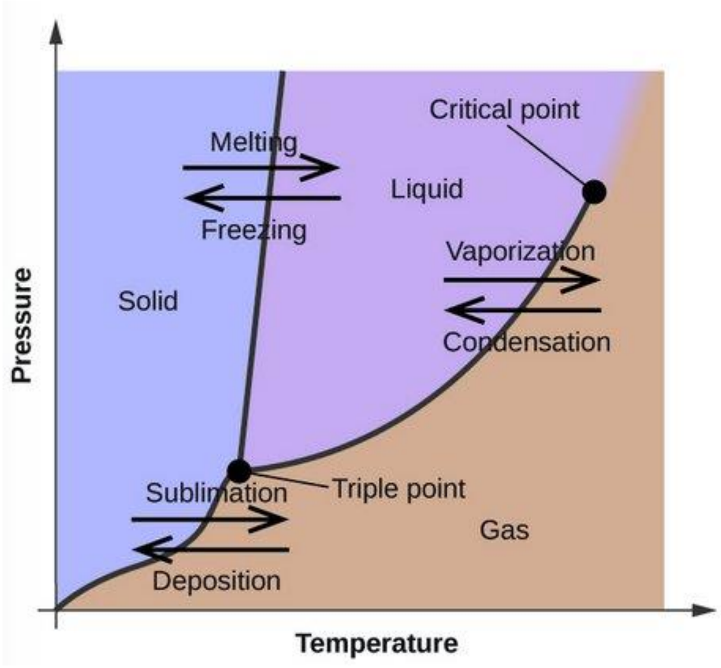
- Removing heat reverses the process, causing some of the substance to transition back to the previous phase.



Phase transitions

At the transition temperature, any transfer of energy as heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium

$$q = \Delta_{\text{trs}} H$$



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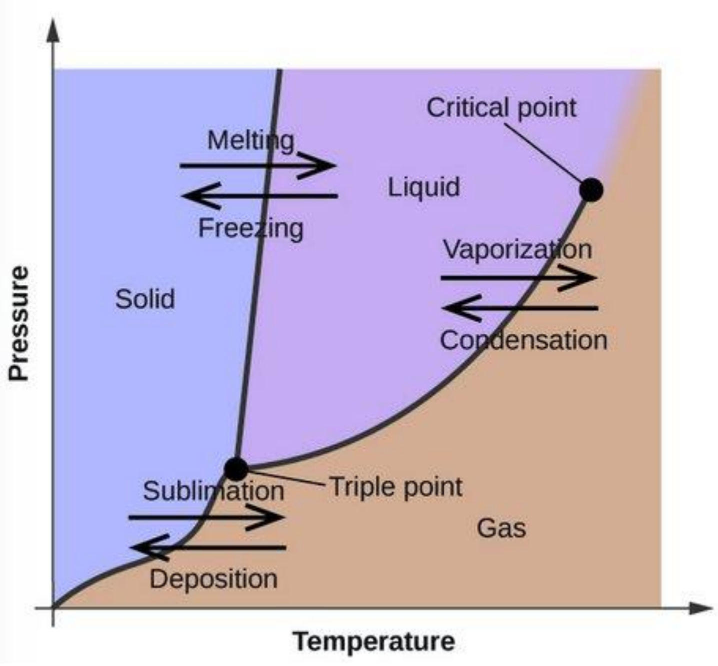

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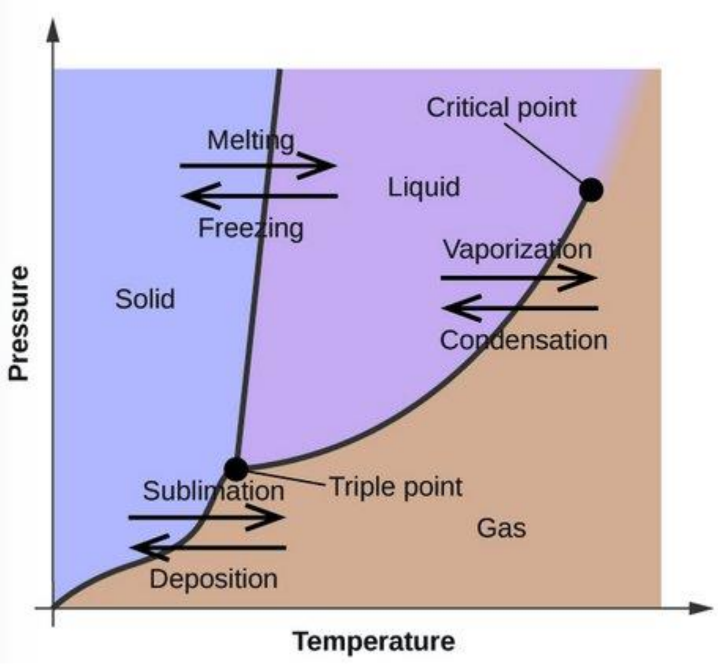

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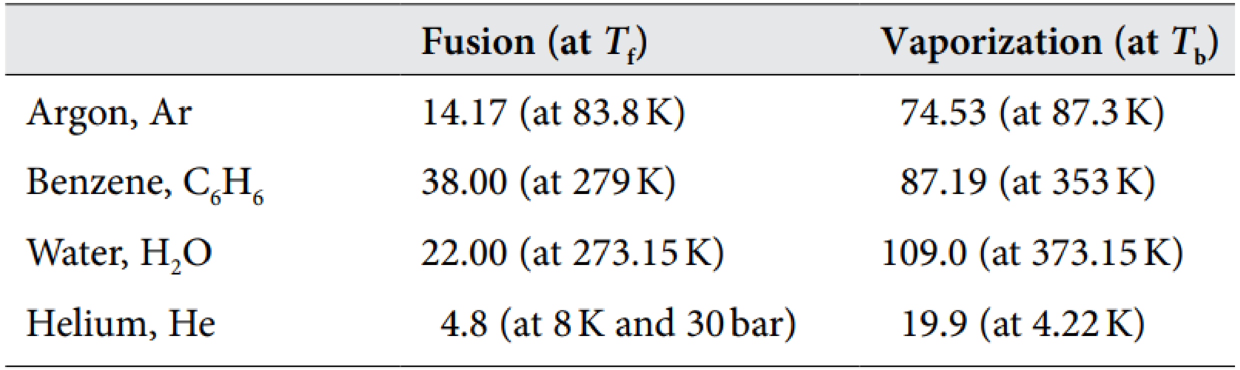

	Fusion (at T_f)	Vaporization (at T_b)
Argon, Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Benzene, C_6H_6	38.00 (at 279 K)	87.19 (at 353 K)
Water, H_2O	22.00 (at 273.15 K)	109.0 (at 373.15 K)
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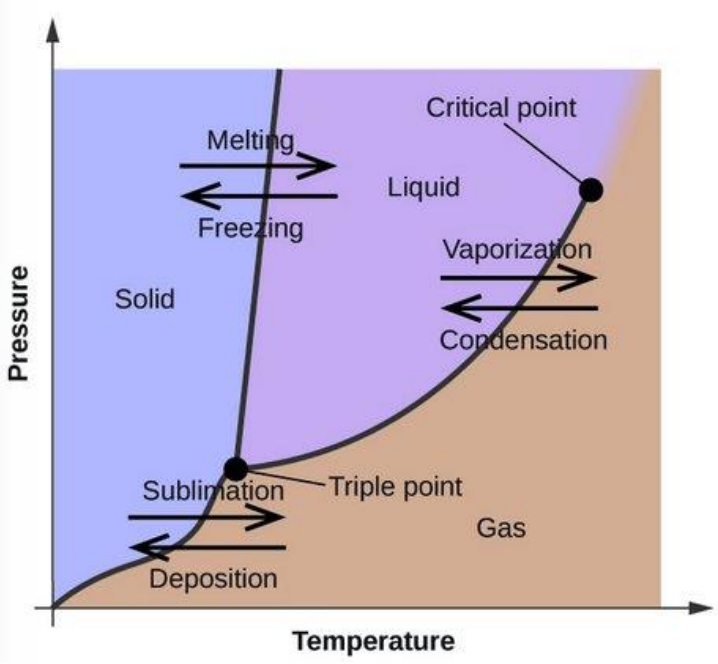

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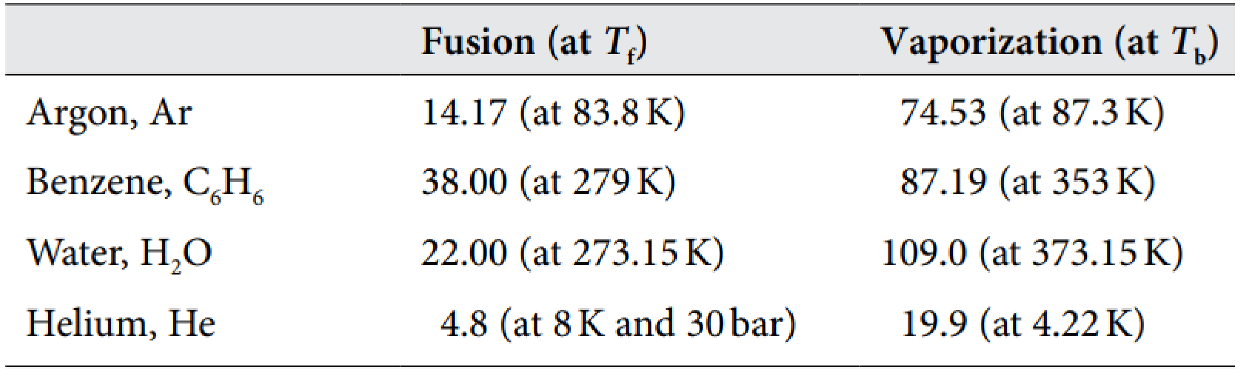

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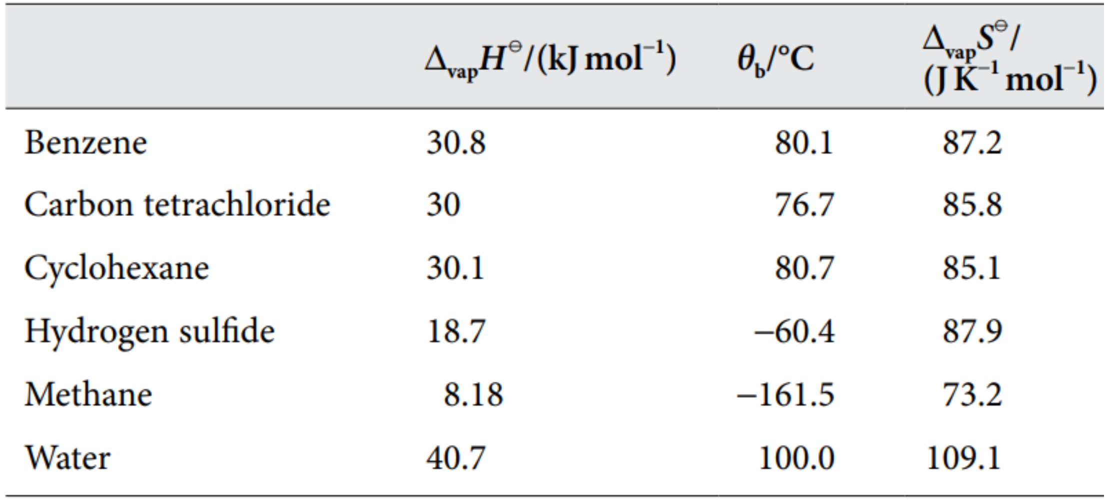

	$\Delta_{vap}H^\ominus$/(kJ mol^{-1})	θ_b/°C	$\Delta_{vap}S^\ominus$/(J K^{-1} mol^{-1})
Benzene	30.8	80.1	87.2
Carbon tetrachloride	30	76.7	85.8
Cyclohexane	30.1	80.7	85.1
Hydrogen sulfide	18.7	−60.4	87.9
Methane	8.18	−161.5	73.2
Water	40.7	100.0	109.1

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$$\begin{aligned}\Delta_{\mathrm{vap}}H^{\ominus} &= (332.4\,\mathrm{K}) \times (85\,\mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= +2.8 \times 10^{4}\,\mathrm{J\,mol^{-1}} = +28\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

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The experimental value is $+29.45\,\text{kJ}\,\text{mol}^{-1}$.

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$$dq_{rev} = dH$$

At constant pressure

$$dH = C_p dT$$

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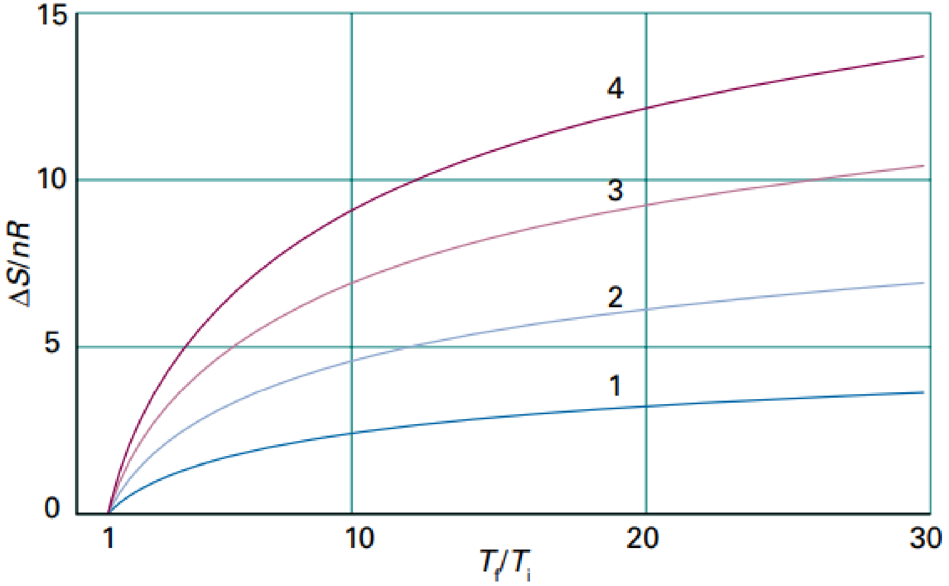
For different Cp/R values



Example

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The molar constant-volume heat capacity of water at 298 K is 75.3 J K^{-1} mol^{-1}. The change in molar entropy when it is heated from 20 °C (293 K) to 50 °C (323 K), supposing the heat capacity to be constant in that range,

What is ΔS?

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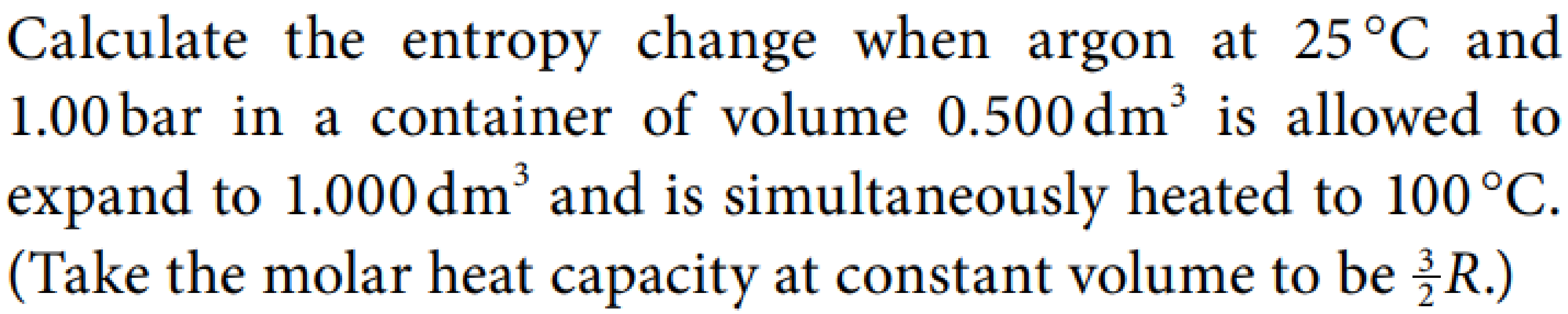

Calculate the entropy change when argon at 25 °C and 1.00 bar in a container of volume 0.500 dm^3 is allowed to expand to 1.000 dm^3 and is simultaneously heated to 100 °C. (Take the molar heat capacity at constant volume to be $\frac{3}{2}R$.)

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$$\Delta S(\mathrm{Step\ 1}) = nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

Combined processes

$$n=\frac{(1.00\times10^{5}\,\mathrm{Pa})\times(0.500\times10^{-3}\,\mathrm{m}^{3})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times298\,\mathrm{K}}=0.0201\ldots\mathrm{mol}$$

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Combined processes

$$n=\frac{(1.00\times10^{5}\,\mathrm{Pa})\times(0.500\times10^{-3}\,\mathrm{m}^{3})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times298\,\mathrm{K}}=0.0201\ldots\mathrm{mol}$$

Calculate the entropy change when argon at 25 °C and 1.00 bar in a container of volume 0.500 dm^3 is allowed to expand to 1.000 dm^3 and is simultaneously heated to 100 °C. (Take the molar heat capacity at constant volume to be $\frac{3}{2}R$.)

$$\Delta S(\text{Step 1})=nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}\quad=0.0201\ldots\mathrm{mol}\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\frac{1.000\,\mathrm{dm}^3}{0.500\,\mathrm{dm}^3}$$

$$\Delta S(\text{Step 2})=nC_{V,m}\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}$$

$$=\tfrac{3}{2}nR\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}$$

Combined processes

$$n = \frac{(1.00\times10^{5}\,\text{Pa})\times(0.500\times10^{-3}\,\text{m}^{3})}{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times298\,\text{K}} = 0.0201\ldots\text{mol}$$

Calculate the entropy change when argon at 25 °C and 1.00 bar in a container of volume 0.500 dm^3 is allowed to expand to 1.000 dm^3 and is simultaneously heated to 100 °C. (Take the molar heat capacity at constant volume to be $\frac{3}{2}R$.)

$$\Delta S(\text{Step 1}) = nR\ln\frac{V_\text{f}}{V_\text{i}} \quad = 0.0201\ldots\text{mol}\times(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\ln\frac{1.000\,\text{dm}^{3}}{0.500\,\text{dm}^{3}}$$

$$\Delta S(\text{Step 2}) = nC_{V,m}\ln\frac{T_\text{f}}{T_\text{i}}$$

$$= \tfrac{3}{2}nR\ln\frac{T_\text{f}}{T_\text{i}} \quad = \tfrac{3}{2}\times(0.0201\ldots\text{mol})\times(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\ln\frac{373\,\text{K}}{298\,\text{K}}$$

Combined processes

$$n=\frac{(1.00\times10^5\,\mathrm{Pa})\times(0.500\times10^{-3}\,\mathrm{m}^3)}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times298\,\mathrm{K}}=0.0201\ldots\mathrm{mol}$$

Calculate the entropy change when argon at 25 °C and 1.00 bar in a container of volume 0.500 dm^3 is allowed to expand to 1.000 dm^3 and is simultaneously heated to 100 °C. (Take the molar heat capacity at constant volume to be $\frac{3}{2}R$.)

$$\Delta S(\text{Step 1})=nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}\quad=0.0201\ldots\mathrm{mol}\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\frac{1.000\,\mathrm{dm}^3}{0.500\,\mathrm{dm}^3}$$

$$\Delta S(\text{Step 2})=nC_{V,m}\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}$$

$$=\tfrac{3}{2}nR\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}\;=\tfrac{3}{2}\times(0.0201\ldots\mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\frac{373\,\mathrm{K}}{298\,\mathrm{K}}$$

$$\Delta S=0.116\ldots\,\mathrm{J\,K^{-1}}+0.0564\ldots\,\mathrm{J\,K^{-1}}=+0.173\,\mathrm{J\,K^{-1}}$$