

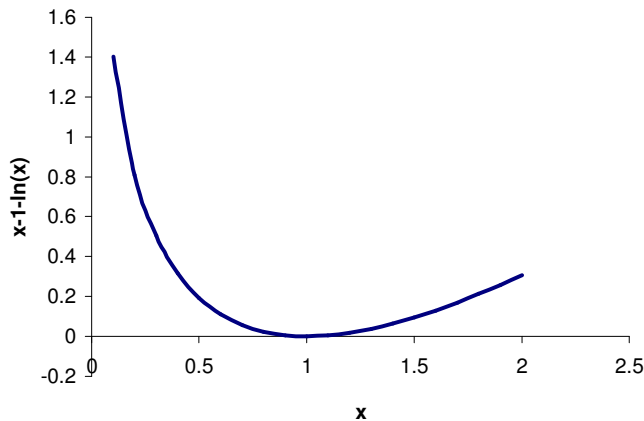
PHY2201 Summary Sheet 3

If a system evolves from an initial to a final state, $\Delta S)_{\text{system}}$ is the SAME, regardless of whether the change is reversible or irreversible (S is a variable of state). The difference lies in $\Delta S)_{\text{surroundings}}$ and hence $\Delta S)_{\text{universe}} [= \Delta S)_{\text{system}} + \Delta S)_{\text{surroundings}}$

e.g. consider heating a mass of water, heat capacity c_v , from temp T_1 to T_2 .

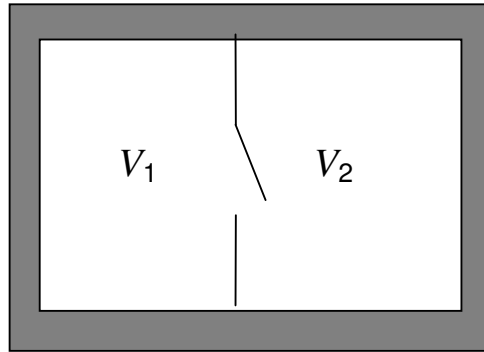
reversible	irreversible
<div style="text-align: center;"> T_1 </div> <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div style="border: 1px solid black; padding: 2px 5px;">T_1</div> <div style="border: 1px solid black; padding: 2px 5px;">$T_1+\Delta T$</div> <div style="border: 1px solid black; padding: 2px 5px;">$T_1+2\Delta T$</div> <div style="border: 1px solid black; padding: 2px 5px;">...</div> <div style="border: 1px solid black; padding: 2px 5px;">T_2</div> </div>	<div style="text-align: center;"> T_1 </div> <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div style="border: 1px solid black; padding: 2px 5px;">T_1</div> <div style="border: 1px solid black; padding: 2px 5px;">T_2</div> </div>
$\Delta S)_{\text{water}} = c_v \ln \frac{T_2}{T_1}$	$\Delta S)_{\text{water}} = c_v \ln \frac{T_2}{T_1}$
$\Delta S)_{\text{surroundings}} = -c_v \ln \frac{T_2}{T_1}$	$\Delta S)_{\text{surroundings}} = -c_v (T_2 - T_1)/T_2$
$\Delta S)_{\text{universe}} = 0$	$\Delta S)_{\text{universe}} = c_v \left(\ln \frac{T_2}{T_1} + \frac{T_1}{T_2} - 1 \right)$

$$\Delta S)_{\text{universe}} = c_v (x - 1 - \ln x) \quad \text{with } x = \frac{T_1}{T_2}$$



So $\Delta S)_{\text{universe}} > 0$ if $T_1 > T_2$ or $T_1 < T_2$.

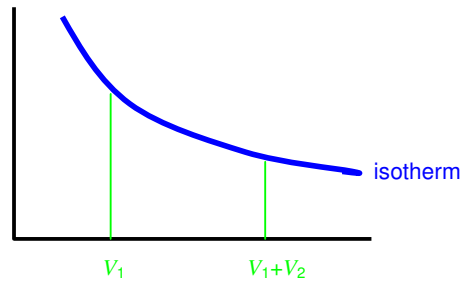
e.g. free (i.e. $\Delta W = 0$), adiabatic (i.e. $\Delta Q = 0$) expansion of an ideal gas.



Expansion is isoenergetic ($\Delta U = \Delta Q + \Delta W = 0$) hence isothermal (for an ideal gas).

Although $\Delta Q = 0$, $\Delta S > 0$ as $\Delta S = \Delta Q/T$ only if change is reversible.

Calculate ΔS by considering idealized, reversible process taking n moles of ideal gas isothermally from volume V_1 to $V_1 + V_2$.



Apply fundamental thermodynamic relationship (FTR)

$$dU = TdS - pdV$$

NB FTR relates variables of state, so is true for ANY change between equilibrium states, reversible or irreversible.

Isoenergetic implies $dU = 0$, hence

$$TdS = pdV$$

$$\therefore \Delta S = \int_{\text{initial}}^{\text{final}} dS = \int_{V_1}^{V_1+V_2} \frac{p}{T} dV$$

n moles of ideal gas obeys equation of state

$$pV = nRT$$

Hence

$$\Delta S = \int_{V_1}^{V_1+V_2} \frac{nR}{V} dV = nR \int_{V_1}^{V_1+V_2} \frac{dV}{V} = nR [\ln V]_{V_1}^{V_1+V_2} = nR \ln \frac{V_1 + V_2}{V_1}$$

Hence $\Delta S > 0$.