The Second Law

\[ \Delta S = \Delta S_{sys} + \Delta S_{sur} > 0 \]
Entropy and heat:

$\Delta S = \int_{i}^{f} \frac{dQ_r}{T}$

Chemical rxns at p,T=const: $\Delta Q_r = \Delta H$

$\Delta S = \frac{\Delta H}{T}$
Why does a cup of coffee cool spontaneously?

no reaction: \( Q_{\text{sur}} = -Q_{\text{sys}} = |Q| \)

\[
\Delta S = \Delta S_{\text{coffee}} + \Delta S_{\text{room}} = -\frac{|Q|}{T_{\text{coffee}}} + \frac{|Q|}{T_{\text{room}}} = |Q| \left( -\frac{1}{370} + \frac{1}{293} \right) > 0
\]
Heat engines: Inherently low efficiency because heat is involved

Max efficiency (Carnot):

\[ e_{\text{max}} = 1 - \frac{T_{\text{env}}}{T_{\text{eng}}} \]

For \( T_{\text{eng}} = 600\text{K} \) and \( T_{\text{env}} = 300\text{K} \) \( e_{\text{max}} = 50\% \)!

1959, West Virginia

2004
Hydrocarbons: most important fuel

Combustion of fuels: exothermic process

Chemistry of heat engines:

$$\text{CH}_4 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$$
Example of the 2nd law violation: spontaneous cooling of a cold object in a hot environment

*It is impossible to construct a device that will transfer heat from a cold reservoir to a hot reservoir in a continuous cycle with no net expenditure of work*

\[
Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)
\]

\[
\Delta S_{sys} > 0
\]

because positional entropy increases as the rxn proceeds from the solid mixture to a solution. Moreover, the number of "independent" particles increases
The Second Law for phase transitions

$$\Delta S = \Delta S_{sys} + \Delta S_{sur} > 0$$

$$\Delta S_{sys} = \frac{\Delta H}{T_{sys}}$$

$$\Delta S_{sur} = -\frac{\Delta H}{T_{sur}}$$

$$\Delta S = \Delta S_{sys} + \Delta S_{sur} = \frac{\Delta H}{T_{sys}} - \frac{\Delta H}{T_{sur}}$$

Endothermic: $\Delta H > 0$, heat in, entropy of the system increases ($\Delta S_{sys} > 0$, $\Delta S_{sur} < 0$)
When spontaneous? $T_{sys} < T_{sur}$. (Think: boiling, melting, etc)

Exothermic: $\Delta H < 0$, heat out, entropy of the system decreases ($\Delta S_{sys} < 0$, $\Delta S_{sur} > 0$)
When spontaneous? $T_{sys} > T_{sur}$. (Think: condensation, crystallization, etc)
Is *protein folding* exothermic or endothermic process?

Folded protein is more ordered system than unfolded - $\Delta S_{sys} < 0$ - occurs spontaneously, thus $\Delta S_{sur} > 0$ - *folding is exothermic*
Calculate $\Delta S$ for boiling water at:

$\Delta H_{\text{vap}} = 40.66$ kJ/mole
$T_b = 373$ K

$T$ of boiling water is equal $T_b = 373$ K regardless of what is a $T$ of environment

$$\Delta S_{\text{sys}} = \frac{\Delta H}{T_{\text{sys}}} = \frac{40.66}{373} = 109 \text{ } J \cdot K^{-1}$$

(a) $273$ K

$$\Delta S_{\text{sur}} = -\frac{\Delta H}{T_{\text{sur}}} = -\frac{40.66}{273} = -148.94 \text{ } J \cdot K^{-1} \quad \Delta S < 0$$

(b) $373$ K

$$\Delta S_{\text{sur}} = -\frac{\Delta H}{T_{\text{sur}}} = -\frac{40.66}{373} = -109 \text{ } J \cdot K^{-1} \quad \Delta S = 0$$

(c) $375$ K

$$\Delta S_{\text{sur}} = -\frac{\Delta H}{T_{\text{sur}}} = -\frac{40.66}{375} = -108.43 \text{ } J \cdot K^{-1} \quad \Delta S > 0$$
In general, can calculate $\Delta S_{\text{rxn}}$ from standard values (at 25C) given in tables:

$$S^0 = S_{298K} - S_{0K} = S_{298K}$$

$$\Delta S_{\text{rxn}} = \sum S^o_{\text{prd}} - \sum S^o_{\text{react}}$$

$$\Delta H_{\text{rxn}} = \sum H^o_f (\text{prd}) - \sum H^o_f (\text{react})$$

$$\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = \Delta S_{\text{rxn}} - \frac{\Delta H}{T_{\text{sur}}} > 0$$
SiO$_2$(s) - $\rightarrow$ Si(s) + O$_2$(g)

$$\Delta S_{rxn} = \sum S^o_{Si(s)} + \sum S^o_{O_2(g)} - \sum S^o_{SiO_2(s)} = 182 J / K > 0$$

But neither sand nor glass decompose spontaneously!
Thus, $\Delta S_{sur} << 0$
Q$_{sur} < 0$ -> very endothermic rxn
\[ \Delta S = \Delta S_{sys} + \Delta S_{sur} = \Delta S_{rxn} - \frac{\Delta H}{T_{sur}} > 0 \]

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