20. Entropy and the Second Law of Thermodynamics

20-1 The Change of Energy Alone is not Sufficient to Determine the Direction of a Spontaneous Process.

Spontaneously processing chemical reactions $\Rightarrow$ always exothermic?

Diffusion of a gas: ΔU and ΔH are nearly 0 $\Rightarrow$ but retrogression never happens.

Examples: mixing of gases, fusion of ice, reaction of $Ba(OH)_2$ and NH_4NO_3, etc.

20-2 Nonequilibrium Isolated Systems Evolve in a Direction that Increases Their Disorder.

Spontaneous process $\rightarrow$ Disorder of the system increases.

$\downarrow$

*tendency for energy to be minimized
*tendency for disorder to be maximized

The first law tells: $\delta q_{\mathrm{rev}} = \mathrm{d}U - \delta W = C_{\mathrm{V}}(T)\,\mathrm{d}T + P\,\mathrm{d}V$

$$= C_{\mathrm{V}}(T)\,\mathrm{d}T + \frac{nRT}{V}\mathrm{d}V$$

$\cdots$ This is not an exact differential. (for q_{rev} depends on paths of integration)

20-2 Nonequilibrium Isolated Systems Evolve in a Direction that Increases Their Disorder. (cont.)

$$C_V(T)\,\mathrm{d}T = \mathrm{d}\int C_V(T)\,\mathrm{d}T + const.$$

$$\frac{nRT}{V}\mathrm{d}V \neq \mathrm{d}\int \frac{nRT}{V}\mathrm{d}V + const.$$ T depends on V.

By dividing by T, this gives:

$$\frac{\delta q_{\mathrm{rev}}}{T} = \frac{C_V(T)}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V$$
$$= \mathrm{d}S$$

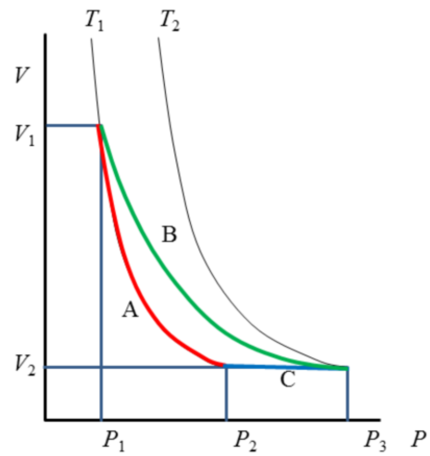
S: entropy $\oint \mathrm{d}S = 0$

S is a state function.

20-3 Unlike q_{rev}, Entropy is a State Function

- $\delta q_{\text{rev,A}} = \frac{nRT_1}{V} \mathrm{d}V$
- $q_{\text{rev,A}} = nRT_1 \ln \frac{V_2}{V_1}$
- $\delta q_{\text{rev,B}} = 0$
- $\delta q_{\text{rev,C}} = C_V(T)\,\mathrm{d}T$

$$q_{\text{rev,B+C}} = \int_{T_1}^{T_2} C_V(T)\,\mathrm{d}T$$



in process B, $\Delta U = \mathrm{d}w$

$$\Rightarrow \int_{T_1}^{T_2} \frac{C_V(T)}{T}\mathrm{d}T = -nR\ln\frac{V_2}{V_1}$$

$$\Delta S = \int_1^2 \frac{\delta q_{\text{rev}}}{T}$$

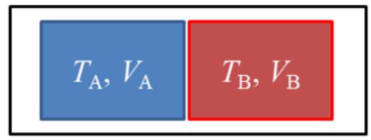
- $\Delta S_A = nR\ln\frac{V_2}{V_1}$
- $\Delta S_B = 0$
- $\Delta S_C = -\int_{T_1}^{T_2} \frac{C_V(T)}{T}\mathrm{d}T$

$$\left.\begin{array}{l}\Delta S_B = 0 \\ \Delta S_C = -\int_{T_1}^{T_2} \frac{C_V(T)}{T}\mathrm{d}T\end{array}\right\} \Delta S_{B+C} = 0 + nR\ln\frac{V_2}{V_1} = \Delta S_A$$

As temperature goes lower, the disorder of a system by δq_{rev} is larger.

20-4 The Second Law of Thermodynamics States that the Entropy of an Isolated System Increases as a Result of Spontaneous Process.

Thermal energy: spontaneously moves from high-T region to low-T region (observed fact).



$U_A + U_B = \text{const.}$
$V_A = \text{const.}, \quad V_B = \text{const.}$
$S = S_A + S_B$

$$\left.\begin{aligned} dU_A &= \delta q_{rev} + \delta W_{rev} = T_A\, dS_A \\ dU_B &= \delta q_{rev} + \delta W_{rev} = T_B\, dS_B \end{aligned}\right\} \Rightarrow dS = dS_A + dS_B = \frac{dU_A}{T_A} + \frac{dU_B}{T_B}$$

$$dU_A = -dU_B$$

$$dS = dU_B\left(\frac{1}{T_B} - \frac{1}{T_A}\right)$$

If $T_B > T_A$, $dU_B < 0$, therefore $dS > 0$
At equilibrated state, $dS = 0$

$$dS = dS_{prod} + dS_{exch} = dS_{prod} + \frac{\delta q}{T} \geq \frac{\delta q}{T}$$

$$\Delta S = \int \frac{\delta q}{T}$$

dS_{prod}: produced inside the system
dS_{exch}: exchange of heat between outside

20-5 The Most Famous Equation of Statistical Thermodinamics is $S = k_B \ln W$

Ensemble of $\mathcal{A}$ pieces of isolated systems

Energy E (degeneracy $\Omega(E)$) $\rightarrow j = 1, 2, \cdots \Omega(E)$

Volume V

Number of particles N

Number of isolated systems in jth state $= a_j$ $\quad \sum_j a_j = \mathcal{A}$

Number of Ways: $W(a_1, a_2, \cdots a_\Omega)! = \dfrac{\mathcal{A}!}{a_1! a_2! \cdots a_\Omega!} = \dfrac{\mathcal{A}!}{\prod_j a_j!}$

Entropy: $S = k_B \ln W$

$\Leftrightarrow \begin{cases} S_{\text{total}} = S_A + S_B \\ W_{AB} = W_A W_B \end{cases}$

S is maximized in equilibrated system. $\Rightarrow$ W is max. $\Rightarrow$ All the n are the same.

$\forall j, a_j = n \;\Rightarrow\; \mathcal{A} = n\Omega$

$$S_{\text{ensemble}} = k_B \ln W = k_B\left[\mathcal{A}\ln\mathcal{A} - \sum_{j=1}^{\Omega} a_j \ln a_j\right] = k_B\left[n\Omega \ln n\Omega - \sum_{j=1}^{\Omega} n \ln n\right] = k_B(n\Omega \ln \Omega)$$

$\because \ln N! \cong N \ln N - N$ (Stirling's formula)

$S_{\text{system}} = k_B \ln \Omega \;\Rightarrow\; S_{\text{ensemble}} = n\Omega S_{\text{system}}$

20-6 We must Always Devise a Reversible Process to Calculate Entropy Changes.

Free expansion of gas

$$\Delta S = \int_1^2 \frac{\delta q_{\mathrm{rev}}}{T}$$

$$\delta W_{\mathrm{rev}} = -P\mathrm{d}V = \frac{nRT}{V}\mathrm{d}V \qquad \Delta S = nR\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = nR\ln\frac{V_2}{V_1}$$

At the interface of metal pieces of different temperature...

Energy: $$C_{\mathrm{V}}(T_{\mathrm{h}} - T) = C_{\mathrm{V}}(T - T_{\mathrm{c}}) \Rightarrow T = \frac{T_{\mathrm{h}} + T_{\mathrm{c}}}{2} \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_{\mathrm{V}}}{T}\mathrm{d}T = C_{\mathrm{V}}\ln\frac{T_2}{T_1}$$

Entropy:

High-T side $$\Delta S_{\mathrm{h}} = C_{\mathrm{V}}\ln\frac{T_{\mathrm{h}} + T_{\mathrm{c}}}{2T_{\mathrm{h}}}$$

Low-T side $$\Delta S_{\mathrm{c}} = C_{\mathrm{V}}\ln\frac{T_{\mathrm{h}} + T_{\mathrm{c}}}{2T_{\mathrm{c}}}$$

total change in entropy

$$\Rightarrow \Delta S = \Delta S_{\mathrm{h}} + \Delta S_{\mathrm{c}} = C_{\mathrm{V}}\ln\frac{(T_{\mathrm{h}} + T_{\mathrm{c}})^2}{4T_{\mathrm{h}}T_{\mathrm{c}}}$$

$(T_{\mathrm{h}} + T_{\mathrm{c}})^2 > 4T_{\mathrm{h}}T_{\mathrm{c}}$, therefore $\Delta S > 0$

20-7 Thermodynamics Gives Us Insight into the Conversion of Heat into Work.

$$\Delta U_{\text{engine}} = W + q_{\text{rev,h}} + q_{\text{rev,c}} = 0$$

$$\Delta S_{\text{engine}} = \frac{\delta q_{\text{rev,h}}}{T_{\text{h}}} + \frac{\delta q_{\text{rev,c}}}{T_{\text{c}}} = 0 \quad \text{(reversible)}$$

$$-W = q_{\text{rev,h}} + q_{\text{rev,c}}$$

Max efficiency $\eta_{\max} = \frac{-W}{q_{\text{rev,h}}} = \frac{q_{\text{rev,h}} + q_{\text{rev,c}}}{q_{\text{rev,h}}} = 1 - \frac{T_{\text{c}}}{T_{\text{h}}} = \frac{T_{\text{h}} - T_{\text{c}}}{T_{\text{h}}}$ ← depends only on T.

20-8 Entropy can be Expressed in Terms of a Partition Function.

$$U = k_{\text{B}} T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \qquad \because \frac{\text{d}\beta}{\text{d}T} = -\frac{1}{k_{\text{B}} T^2}$$

$$P = k_{\text{B}} T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}$$

$$S_{\text{ensemble}} = k_{\text{B}} \ln \frac{\mathcal{A}!}{\prod_j a_j!} \cong k_{\text{B}} \left[\mathcal{A} \ln \mathcal{A} - \sum_{j=1}^{\Omega} a_j \ln a_j \right] = \mathcal{A} S_{\text{system}}$$

20-8 Entropy can be Expressed in Terms of a Partition Function. (cont.)

Probability that the state of the system is j: $p_j = \dfrac{a_j}{\mathcal{A}}$

$$S_{\text{ensemble}} = -\mathcal{A}k_B \sum_j p_j \ln p_j \;\Rightarrow\; S_{\text{system}} = -k_B \sum_j p_j \ln p_j$$

$$p_j = p_j(N,V,\beta) = \frac{\exp[-\beta E_j(N,V)]}{Q(N,V,\beta)}$$

then,

$$S_{\text{system}} = -k_B \sum_j \frac{\exp[-\beta E_j]}{Q}(-\beta E_j - \ln Q) = \frac{U}{T} + k_B \ln Q = k_B T\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q$$

Monoatomic ideal gas in the ground state: $Q = Q(N,V,T) = \dfrac{1}{N!}\left(\dfrac{2\pi m k_B T}{h^2}\right)^{3N/2} V^N g_{\text{el}}$

Entropy per 1 mol:

$$\overline{S} = \frac{3}{2}R + R\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \overline{V} g_{\text{el}}\right] - k_B \ln N_A!$$

$$= \frac{5}{2}R + R\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{\overline{V} g_{\text{el}}}{N_A}\right]$$

20-9 The Molecular Formula $S = k_B \ln W$ is Analogous to Thermodynamic Formula $dS = \delta q_{rev} / T$.

$$S = -k_B \sum_j p_j \ln p_j$$

By differentiating by p_j, $\quad dS = -k_B \sum_j (dp_j + \ln p_j dp_j)$

$\sum_j dp_j = 0$, therefore $\quad dS = -k_B \sum_j \ln p_j dp_j$

By substituting $\ln p_j$ with $p_j = \dfrac{\exp[-\beta E_j]}{Q}$,

$$dS = -k_B \sum_j [-\beta E_j - \ln Q] dp_j$$

$$\sum_j [\ln Q] dp_j = \ln Q \sum_j dp_j = 0$$

then, $\quad dS = -\beta k_B \sum_j E_j dp_j$

$\sum_j E_j dp_j$ is energy transferred among the system as heat during a reversible process.

$$\Rightarrow dS = -\beta k_B \delta q_{rev} = \frac{\delta q_{rev}}{T}$$