CHEMISTRY 24a
Winter Quarter 1997
Instructor: Chan
Lecture 4

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Reading Assignment

Eisenberg & Crothers: Chapter 4

Second Law of Thermodynamics

For a reversible process, $dS = \frac{dQ_{rev}}{T}$

For an irreversible process, $dS > \frac{dQ_{irrev}}{T}$

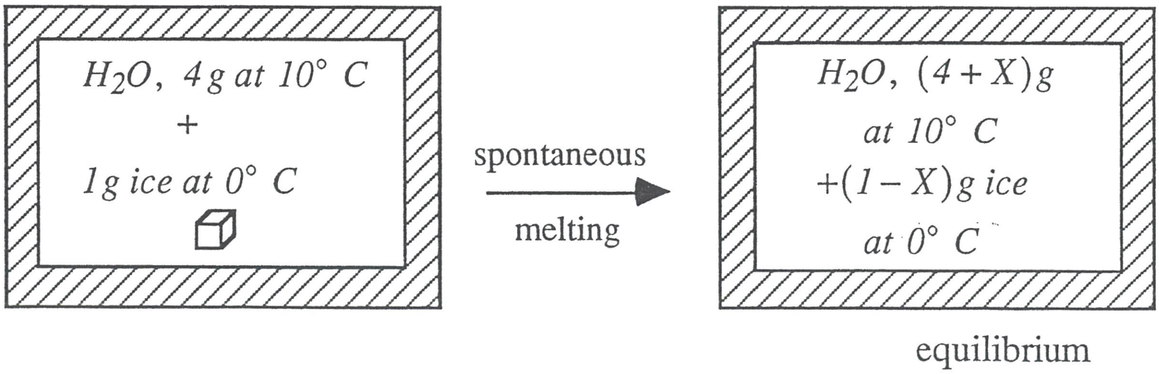
or $dS \geq \frac{dQ}{T}$

$dQ \equiv$ *heat input to* **system**

$T \equiv$ *temperature of* **system** *(absolute)*

(Similar expression for surroundings!)

A concrete example involving heat transfer only



ΔE process = 0

ΔS process = ?

- **Equilibrium**

How many grams of ice must melt to reach equilibrium?

Specific heat of water $= 1 \text{ cal g}^{-1}\,°\text{C}^{-1}$

$\Delta H_{\text{fusion}} = 80 \text{ cal g}^{-1}$

To attain equilibrium, must melt X grams of ice to cool 4 grams of H_2O from 10°C to 0°C.

or $(X \text{ g})(80 \text{ cal g}^{-1}) = (4\text{g})(1 \text{ cal g}^{-1}°\text{C}^{-1})(10°\text{C})$

$80\,X = 40$ $\quad x = 0.5\text{g}$

- **So process**

$$\begin{array}{c} H_2O,\ 4 \text{ grams at } 10°\text{C} \\ + \\ 1 \text{ gram ice at } 0°\text{C} \end{array} \longrightarrow \begin{array}{c} H_2O,\ (4.5) \text{ grams} \\ \text{at } 0°\text{C} \\ +0.5 \text{ gram ice at } 0°\text{C} \end{array}$$

- $\Delta S_{\text{process}} = ?$

$$\Delta S_{ice} = \int \frac{dQ_{rev}}{T_{ice}} \quad \underset{constant\ T}{\overset{melting}{\Rightarrow}} \quad \frac{Q_{rev}}{T_{ice}} = \frac{0.5g\ 80\ cal\ g^{-1}}{273K}$$

$$= 0.1465\ cal\ K^{-1}$$

$$\Delta S_{H_2O} = \int \frac{dQ_{rev}}{T_{water}} = \int_{283}^{273} \frac{CdT}{T_{water}} = 4g.\ 1\ cal\ g^{-1}\,°C^{-1} \int_{283}^{273} \frac{dT}{T_{water}}$$

$$= 4\ln\left(\frac{273}{283}\right)\ cal\ K^{-1} = -0.1439\ cal\ K^{-1}$$

$$\Delta S_{\text{process}} = \Delta S_{\text{ice}} + \Delta S_{H_2O}$$

$$= (0.1465 - 0.1439) \text{ cal K}^{-1}$$

$$= 0.0026 \text{ cal K}^{-1}$$

$$= (0.0026)\,(4.184 \text{ J K}^{-1})$$

$$= 0.0109 \text{ J K}^{-1}$$

1 kcal mol^{-1} = 4.184 kJ mol^{-1}
1 kcal = 4.184 kJ
1 cal = 4.184 J

Entropy changes due to change in volume

consider $\boxed{\text{ideal}}$ gas & reversible isothermal expansion

Recall First Law: $dE = dQ - P_{ext}dV$

Reversible process $\Rightarrow$ $dE = dQ_{rev} - P_{system}dV$

$$= TdS - PdV$$

Isothermal expansion of ideal gas $\Rightarrow$ dE = 0
E(T) only

Therefore $TdS = PdV = \dfrac{nRT}{V}dV$

or $dS = \dfrac{nR}{V}dV$

$$\Delta S = \int_{V_i}^{V_f} \frac{nR}{V}\,dV = nR\ln\frac{V_f}{V_i}$$

This result suggests that:

$$S_{\substack{\text{ideal gas}\\ \text{perfect gas}}} = constant + nRlnV$$

However, since $pV = nRT$ *here,*

$$S_{\substack{\text{ideal gas}\\ \text{perfect gas}}} = constant + nRln\left(\frac{nRT}{P}\right)$$

$$= f(n,T) - nRlnP\ gas$$

So entropy of ideal gas <u>increases</u> with an isothermal volume <u>increase</u>.

- **Statement is true in general.**

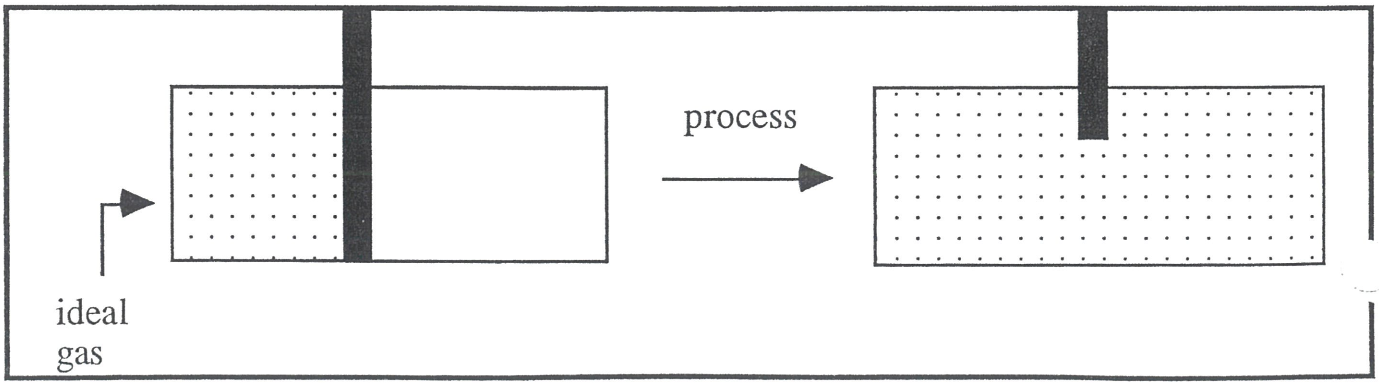
<u>Important Implication of Result</u> - <u>Entropy of Mixing</u>

Pure substance S(N,T,V) or S(n,T,V) <u>state function</u>

Constant mass (closed system S(T,V)

convenient independent variables

- **So can calculate ΔS for one of the processes considered earlier.**



N_i, T, V_i $\qquad\qquad\qquad\qquad$ $N_f,\ T,\ V_f$

$(or\ n_i)$ ↑ $\qquad\qquad\qquad\qquad$ $or\ (n_f)$

volume accessible
to gas molecules

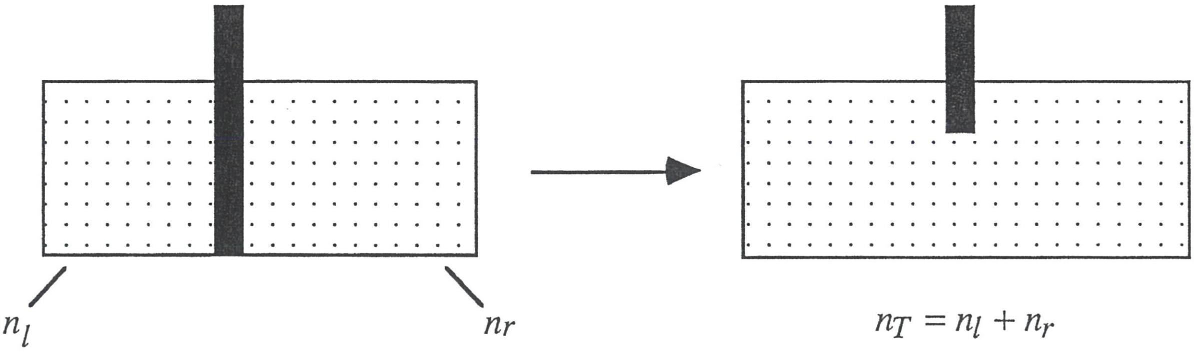
$n_f = n_i \quad = n$

$$\therefore \Delta S_{process} = nR\ln\frac{V_f}{V_i}$$

depends on initial
and final states only

<u>S is a state function!</u>

- **What happens when both sides of the chamber are filled by the same ideal gas at the same pressure?**



T_i
$P_l^i = \frac{n_l RT}{V_l^i}$
V_l^i

T_i
$P_r^i = \frac{n_r RT}{V_r^i}$
V_r^i

$n_T = n_l + n_r$
$T_f = T_i = T$
$P_f = \frac{(n_l + n_r)}{V_T} RT$
$V_f = V_l^i + V_r^i$

<u>Now</u> $\quad P_f = P_l^i = P_r^i$

because $\quad V_f = V_l^i + V_r^i = \frac{n_l RT}{P_l^i} + \frac{n_r RT}{P_r^i} = \frac{(n_l + n_r)RT}{P_l^i}$

<u>cf</u> $\quad V_f = \frac{(n + n_r)RT}{P_f}$

<u>Δ Sprocess</u>

S is an extensive property $\quad\Rightarrow\quad$ $S(n,T,V)\ or\ S(n,T,P)$

Will later show that

$$\underset{\textit{ideal gas}}{S_{translation}} = nR\left\{f(T) + \ln\frac{V}{n}\right\}$$

Note that f(T) & g(T) depend on the nature of the molecules as well, e.g. mass

or $$\underset{\textit{ideal gas}}{S_{translation}} = nR\{g(T) - \ln P\}$$

from which it follows that

$$\underset{\substack{\textit{expansion}\\ \textit{for n moles}\\ \textit{of ideal gas}}}{\Delta S_{isothermal}} = nR\ln\frac{V_f}{V_i} \quad \textit{as shown earlier.}$$

Now for one process here,

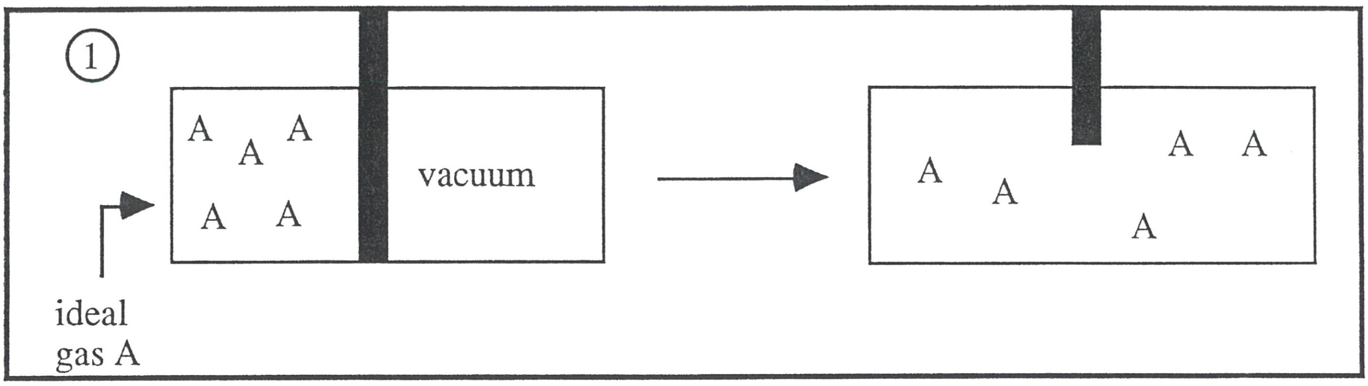
$$\begin{aligned}
\Delta S_{process} &= S\left(n_T, T, V_f\right) - S\left(n_l, T, V_l^i\right) - S\left(n_r, T, V_r^i\right)\\
&= n_T R\left\{f(T) + \ln\frac{V_f}{n_T}\right\}\\
&\quad -nR\left\{f(T) + \ln\frac{V^i}{n}\right\}\\
&\quad -n_r R\left\{f(T) + \ln\frac{V_r^i}{n_r}\right\}\\
&= 0 \qquad \textit{because } \frac{V_f}{n_T} = \frac{V_l^i}{n} = \frac{V_r^i}{n_r}\\
&\qquad\qquad \textit{or} \qquad P_f = P_l^i = P_r^i
\end{aligned}$$

Could have obtained the same result as follows:

$$\begin{aligned}
\Delta S_{process} &= S\left(n_T, T, P_f\right) - S\left(n_e, T, P^i\right) - S\left(n_r, T, P_r^i\right)\\
&= n_T R\left\{g(T) - \ln P_f\right\}\\
&\quad -n_l R\left\{g(T) - \ln P_l^i\right\}\\
&\quad -n_r R\left\{g(T) - \ln P_r^i\right\}\\
&= 0 \qquad \textit{because } P_f = P_l^i = P_r^i
\end{aligned}$$

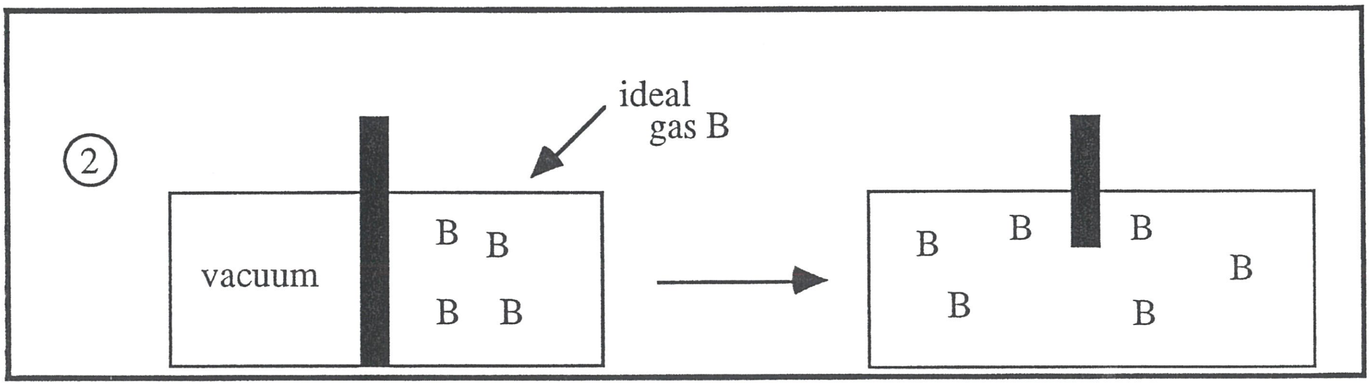
- **What happens when the two sides of the chamber are initially occupied by a different gas at the same pressure?**

Process equivalent to sum of following two <u>processes</u>.



n_A,
V_i^A
$T_i = T$
$P_i^A = \frac{n_A RT}{V_i^A}$

n_A
$V_f = V_T$
$T_f = T$
$P_f^A = \frac{n_A RT}{V_T}$



Volume or phase space accessible to each of the gases per mole has increased!!

n_B
V_i^B
$T_i = T$
$P_i^B = \frac{n_B RT}{V_i^B}$

n_B
$V_f = V_T$
$T_f = T$
$P_f^B = \frac{n_B RT}{V_T}$

$$\Delta S_{process} = \Delta S_A + \Delta S_B$$

$$= n_A R \ln\left(\frac{V_T}{V_i^A}\right)\left(\cancel{\frac{n_A}{n_A}}\right) + n_B R \ln\left(\frac{V_T}{V_i^B}\right)\left(\cancel{\frac{n_B}{n_B}}\right)$$

Initial pressures same $\Rightarrow$ $\dfrac{n_A}{V_i^A} = \dfrac{n_B}{V_i^B}$

<u>Final pressure</u>

same

$$P_f = P_f^A + P_f^B = \frac{n_A RT}{V_T} + \frac{n_B RT}{V_T} = \left[\left(\frac{n_A}{V_i^A}\right)\frac{V_i^A}{V_T} + \left(\frac{n_B}{V_i^B}\right)\frac{V_i^B}{V_T}\right]RT.$$

$$= \frac{n_A}{V_i^A}\frac{(V_i^A + V_i^B)}{V_T}.RT = \frac{n_A}{V_i^A}.RT = P_i^A = P_i^B$$

<u>So</u> $\dfrac{n_A + n_B}{V_T} = \dfrac{n_A}{V_i^A} = \dfrac{n_B}{V_i^B}$

or $\boxed{\dfrac{V_T}{V_i^A} = \dfrac{n_A + n_B}{n_A} = X_A^{-1}}$

and $\boxed{\dfrac{V_T}{V_i^B} = \dfrac{n_A + n_B}{n_B} = X_B^{-1}}$

$$\therefore\ \Delta S_{process} = -n_A R \ln X_A - n_B R \ln X_B$$

$$= -n_T\left[X_A R \ln X_A + X_B R \ln X_B\right] \text{ entropy of mixing}$$

for ΔG mixing, this requires a $\underline{T}$ component;
only valid for ideal gases / soln.

- **General Formula for Entropy of Mixing of Ideal Gases**

$$\boxed{\Delta S_{mixing} = -n_T R \sum_i X_i \ln X_i}$$

(if per mole of mixture, $n_T = 1$)

components in mixture

Entropy Changes in General

$$\Delta S_{process} = \Delta S_{system} + \Delta S_{surroundings}$$

Must always include $\Delta S_{system} + \Delta S_{surroundings}$.

For each part (i.e., system or surroundings), can take advantage that S ≡ entropy is a state function; i.e., $S(n,T,V)$ or $S(n,T,P)$

First Law

$$dE = dQ - P_{ext}dV \qquad \text{(general)}$$

$$dE = dQ_{rev} - PdV \qquad \text{(reversible)}$$

$$\boxed{dE = TdS - PdV \qquad \text{general}}$$

or $$dS = \frac{dE + PdV}{T}$$

Since we may express dE further, e.g.

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

$$= C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

we have $$\boxed{dS = \frac{C_V}{T} dT + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV}$$ completely general!

One equation for system and another for surroundings.

- **For ideal gas.**

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \;\&\; P = \frac{nRT}{V},\; so\; \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] = \frac{nR}{V}$$

$$\therefore dS = \frac{C_V}{T}dT + \frac{nR}{V}dV \qquad \text{(ideal gas)}$$

and $$\Delta S_{ideal\ gas} = \int_{T_i}^{T_f}\frac{C_V}{T}dT + \int_{V_i}^{V_f}\frac{nRT}{V}dV$$

$$= C_V ln\left(\frac{T_f}{T_i}\right) + nRln\left(\frac{V_f}{V_i}\right)$$

- **For constant pressure processes, more convenient to recast above in terms of enthalpy H.**

$$dE = TdS - pdV \qquad \text{general}$$

<u>Now</u> $$dH = dE + pdV + VdP \qquad \text{general}$$

Combining $$dH = TdS + Vdp$$

Since we may express dH further, e.g.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\boxed{dS = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP}$$

<u>For a constant pressure process, then</u> : <u>ie</u>, $dP = 0$

$$\Delta S = \int_{T_i}^{T_f}\frac{C_p}{T}dT$$

Note that if phase changes take place during process, there exist singularities in C_P, but

$$\Delta S_{\substack{phase\\ transition}} = \frac{1}{T_{transition}}\int_{transition} C_P dT = \frac{\Delta H_{transition}}{T_{transition}}$$

Cyclic Processes

For system that has undergone a complete cycle,

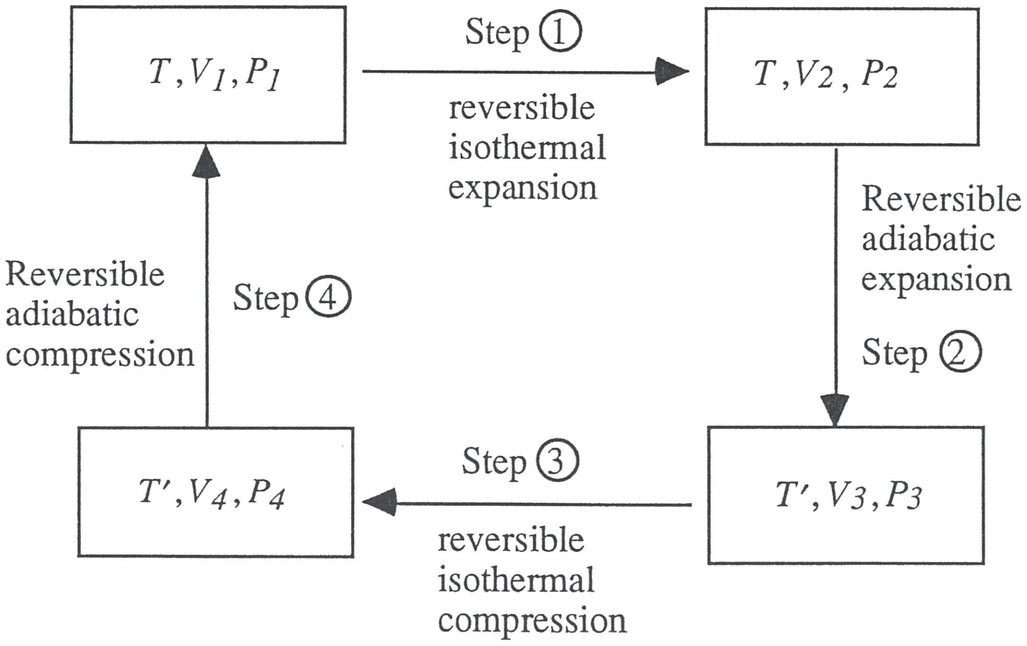
$\Delta S_{system} = 0$ since $\oint dS = 0$ & S is a state function.

But $\Delta S_{system} + \Delta S_{surroundings} = \oint d_{system} + \Delta S_{surrounding}$

≥ 0 *depending upon whether the process is reversible or irreversible*

or $\oint dS_{system + surrounding} \geq 0$

Example (p. 89-91 text) of a cyclic process



$\Delta S_{(2)} = \int \frac{dQ_{rev}}{T}$

$= 0$

no heat input to system

		$\Delta S_{step}^{\ system}$
Step 1	Reversible isothermal expansion	$nRln\left(\frac{V_2}{V_1}\right)$
Step 2	Reversible adiabatic expansion	0
Step 3	Reversible isothermal compression	$nRln\left(\frac{V_4}{V_3}\right)$
Step 4	Reversible adiabatic compression	0

$$\Delta S_{\substack{gas\\system}} = nR\ln\left(\frac{V_2}{V_1}\right) + nR\ln\left(\frac{V_4}{V_3}\right)$$

Need $\frac{V_2}{V_1}$ *and* $\frac{V_4}{V_3}$

From step 2, adiabatic reversible expansion

$$\left(\frac{T'}{T}\right) = \left(\frac{V_2}{V_3}\right)^{nR/C_V}$$

From step 4, adiabatic reversible compression

$$\left(\frac{T}{T'}\right) = \left(\frac{V_4}{V_1}\right)^{nR/C_V}$$

or $$\frac{V_2}{V_3} = \frac{V_1}{V_4}$$

or $$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\therefore \Delta S_{\substack{gas\\system}} = nRln\left(\frac{V_2}{V_1}\right) - nRln\left(\frac{V_3}{V_4}\right) = 0$$

Now $Q_{system} = Q_{step\ 1} + Q_{step\ 2} + Q_{step\ 3} + Q_{step\ 4}$

$$= nRTln\left(\frac{V_2}{V_1}\right) + 0 + nRT'ln\left(\frac{V_4}{V_3}\right) + 0$$

$$= nRTln\left(\frac{V_2}{V_1}\right) + nRT'ln\left(\frac{V_4}{V_3}\right) \qquad \neq 0$$

This result probably prompted Clausius to introduce S and $dS = \frac{dQ_{rev}}{T}$.