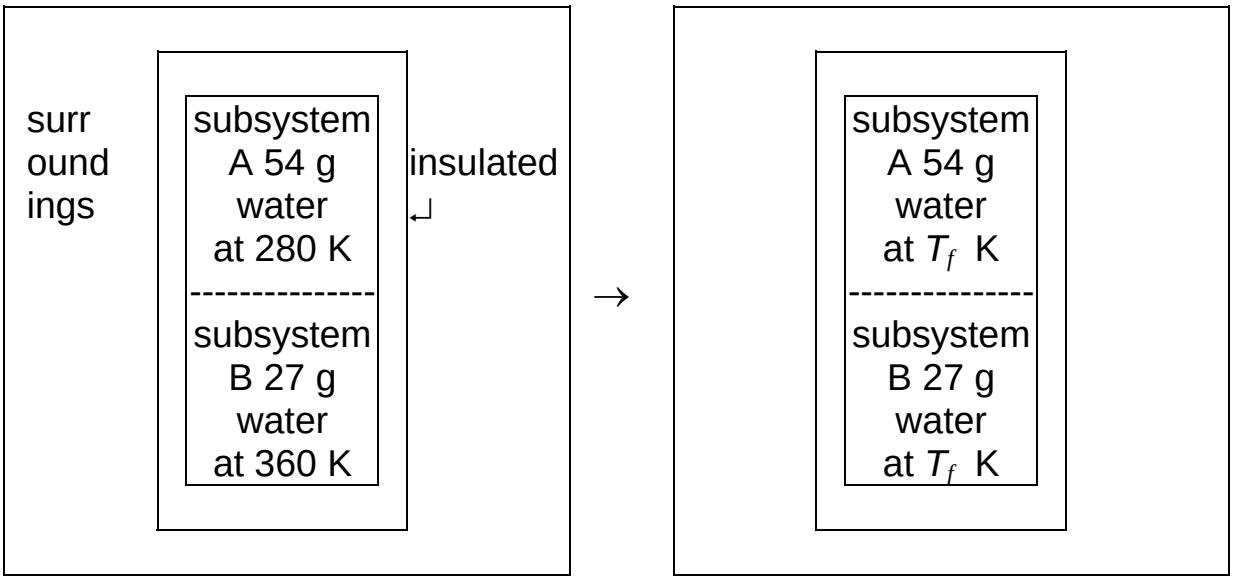
Problem: ***Calculate the entropy change*** that results from mixing 54.0 g of water at 280 K with 27.0 g of water at 360 K in a vessel whose walls are perfectly insulated from the surroundings. ***Is this a spontaneous process?***

Consider the heat capacity of liquid water a constant over the temperature range from 280 K to 360 K and to have the value 4.18 J K^{-1} g^{-1}.

Draw a picture
Look inside the system only, and imagine the system to be in two parts, separated by a thermally conducting interface, each part doing its own system accounting of **q** (and ***w*** , had there been any work).
Consider each part reversibly heating or cooling the other part.



initial final

$\mathbf{q}_{surr} = 0$ since insulated, no **q** can pass across the boundary between system and its surroundings

$\mathbf{q}_{system} = 0$ since insulated, no **q** can pass across the boundary between system and its surroundings

Recall the definitions of concepts and terms:

Second law of thermodynamics,

$d\boldsymbol{S} = đ\mathbf{q}_{rev}/T$

definition of heat capacity:

$đ\mathbf{q} = C\, dT$

$\mathbf{q}_{A\ system}$

$= 54.0\ g \times 4.18\ J\ K^{-1}\ g^{-1} \times (T_f - 280)$

$\mathbf{q}_{B\ system}$

$= 27.0\ g \times 4.18\ J\ K^{-1}\ g^{-1} \times (T_f - 360)$

$T_f = ?$

$\mathbf{q}_{\text{system}} = 0 = \mathbf{q}_{\text{A system}} + \mathbf{q}_{\text{B system}}$

$= 54.0\ \text{g} \times 4.18\ \text{J K}^{-1}\ \text{g}^{-1} \times (T_f - 280) +$

$27.0\ \text{g} \times 4.18\ \text{J K}^{-1}\ \text{g}^{-1} \times (T_f - 360)$

Solve for T_f : $T_f = 306.67\ \text{K}$

$d\boldsymbol{S} = đ\mathbf{q}_{\text{rev}}/T = C\,dT/T$. Integrating gives $\Delta \boldsymbol{S}_{\text{A}} = C \ln (T_f / T_i)$

$\Delta \boldsymbol{S}_{\text{A system}}$

$= 54.0\ \text{g} \times 4.18\ \text{J K}^{-1}\ \text{g}^{-1}$

$\times \ln (306.67/280)$

$= +20.54\ \text{J K}^{-1}$

$\Delta \boldsymbol{S}_{\text{B system}}$

$= 27.0\ \text{g} \times 4.18\ \text{J K}^{-1}\ \text{g}^{-1}$

$\times \ln (306.67/360)$

$= -18.10\ \text{J K}^{-1}$

$\Delta S_{system} = \Delta S_{A\ system} + \Delta S_{B\ system}$
$= +20.54 - 18.10 = +2.44\ \ J\ K^{-1}$

$\Delta S_{surr} = 0$ since no **q** passed across the insulated boundary

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$
$= +2.44\ \ J\ K^{-1}$

spontaneous process ? YES
because $\Delta S_{universe} > 0$

Example:

Consider the following cycle using 1 mole of an ideal gas, initially at 25° C and 1 atm pressure.

Step 1: Isothermal expansion against zero pressure to double the volume.

Step 2. Isothermal, reversible compression from ½ atm to 1 atm

Questions:

(a) Calculate the values of $\oint d\boldsymbol{q}/T$

(b) Calculate $\Delta \boldsymbol{S}$ for step 2

(c) Find $\Delta \boldsymbol{S}$ for step 1

EXAMPLE:

1. Calculate the change in entropy when 50 g of water at 80°C is poured into 100 g of water at 10°C in an insulated vessel given that the molar heat capacity of liquid water is 75.5 J K^{-1} mol^{-1} at 1 atm.

EXAMPLE:

2. Calculate the difference in molar entropy (a) between liquid water and ice at -5°C, (b) between liquid water and its vapor at 95°C and 1.00 atm. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

Given: The differences in heat capacities on melting and on vaporization are 37.3 J K^{-1} mol^{-1} and - 41.9 J K^{-1} mol^{-1}, respectively.

$\Delta_{fus}\boldsymbol{H}$ = 6.01 kJ mol^{-1} at 273 K

$\Delta_{vap}\boldsymbol{H}$ = 40.7 kJ mol^{-1} at 373 K

This means

$C_p(liq) - C_p(s) = 37.3$ J K^{-1} mol^{-1}

$C_p(g) - C_p(liq) = -41.9$ J K^{-1} mol^{-1}

Example:

Consider the following cycle using 1 mole of an ideal gas, initially at 25° C and 1 atm pressure.

Step 1: Isothermal expansion against zero pressure to double the volume.

Step 2. Isothermal, reversible compression from ½ atm to 1 atm

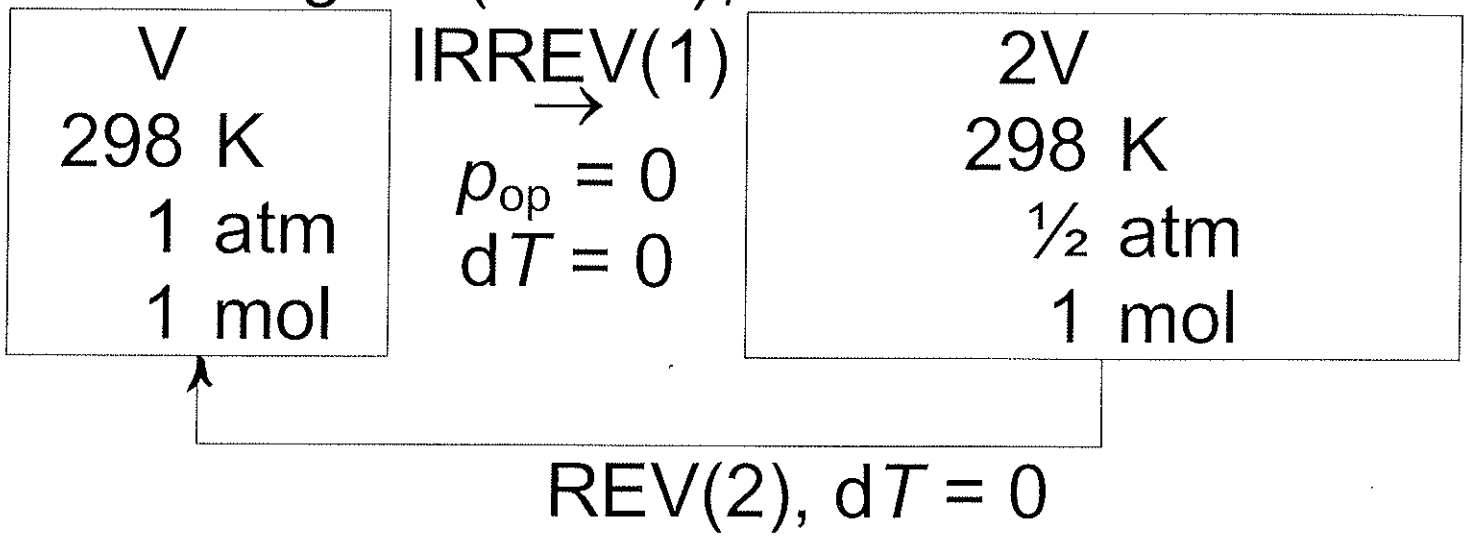
Questions:

(a) Calculate the values of $\oint d\boldsymbol{q}/T$

(b) Calculate $\Delta \boldsymbol{S}$ for step 2

(c) Find $\Delta \boldsymbol{S}$ for step 1

ideal gas $(\partial \boldsymbol{U}/\partial V)_T = 0$



Step1 +Step 2 = a cycle

$d\boldsymbol{U} = (\partial \boldsymbol{U}/\partial T)_V dT + (\partial \boldsymbol{U}/\partial V)_T dV$

Since $dT = 0$ and $(\partial \boldsymbol{U}/\partial V)_T = 0$ for both step 1 and step 2,

$\Delta \boldsymbol{U}_1 = 0$, $d\boldsymbol{q}_{IRREV} = d\boldsymbol{W}$, $d\boldsymbol{W} = -0 \bullet dV$,

$\therefore d\boldsymbol{q}_{IRREV} = 0$

$\Delta \boldsymbol{U}_2 = 0$, $d\boldsymbol{q}_{REV} = -\, d\boldsymbol{W}_{REV} = RT/V \bullet dV$

(a) $\oint d\boldsymbol{q}\,/T = 0 + R\ln(1/2) = -1.38$ cal K^{-1}

(b) $\Delta \boldsymbol{S}_2 = \boldsymbol{q}_{REV}/T = -1.38$ cal K^{-1}

$\Delta \boldsymbol{S}_{cycle} = 0 = \Delta \boldsymbol{S}_1 + \Delta \boldsymbol{S}_2 = \Delta \boldsymbol{S}_1 - 1.38$

(c) $\Delta \boldsymbol{S}_1 = +1.38$ cal K^{-1}

EXAMPLE:

1. Calculate the change in entropy when 50 g of water at 80°C is poured into 100 g of water at 10°C in an insulated vessel given that the molar heat capacity of liquid water is 75.5 J K^{-1} mol^{-1} at 1 atm.

1. Vessel is insulated, net $q = 0$.
Find the common final temperature T_f .
$q = q_1 + q_2 = 0$ (insulated, therefore an adiabatic process)
Since C_p is given as a constant,
$q_1 = n_1 C_p [T_f - T_{i(1)}]$
$q_2 = n_2 C_p [T_f - T_{i(2)}]$
Do the algebra to get
$T_f = \{n_1 T_{i(1)} + n_2 T_{i(2)}\} / \{n_1 + n_2\}$
$= \{(1/3)\times 353\text{K} + (2/3)\times 283\text{K}\} = 306\text{K}$

By definition,
$\Delta \boldsymbol{S}_1 = \int d\boldsymbol{S} = \int dq_{rev}/T = n_1 \int C_p \, dT/T$
$= n_1 C_p \, ln[T_f/T_{i(1)}]$
$\Delta \boldsymbol{S}_2 = n_2 C_p \, ln[T_f/T_{i(2)}]$
$\Delta \boldsymbol{S} = \Delta \boldsymbol{S}_1 + \Delta \boldsymbol{S}_2$
$\Delta \boldsymbol{S} = 75.5 \text{ J K}^{-1} \text{ mol}^{-1} \times$
$\{ [50 \text{ g}/18.02 \text{ g mol}^{-1}] \ln(306/353)$
$+[100 \text{ g}/18.02 \text{ g mol}^{-1}] \ln(306/283) \}$
$= +2.8 \text{ J K}^{-1}$.

EXAMPLE:

2. Calculate the difference in molar entropy (a) between liquid water and ice at -5°C, (b) between liquid water and its vapor at 95°C and 1.00 atm. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

Given: The differences in heat capacities on melting and on vaporization are $37.3\ J\ K^{-1}\ mol^{-1}$ and $-41.9\ J\ K^{-1}\ mol^{-1}$, respectively.

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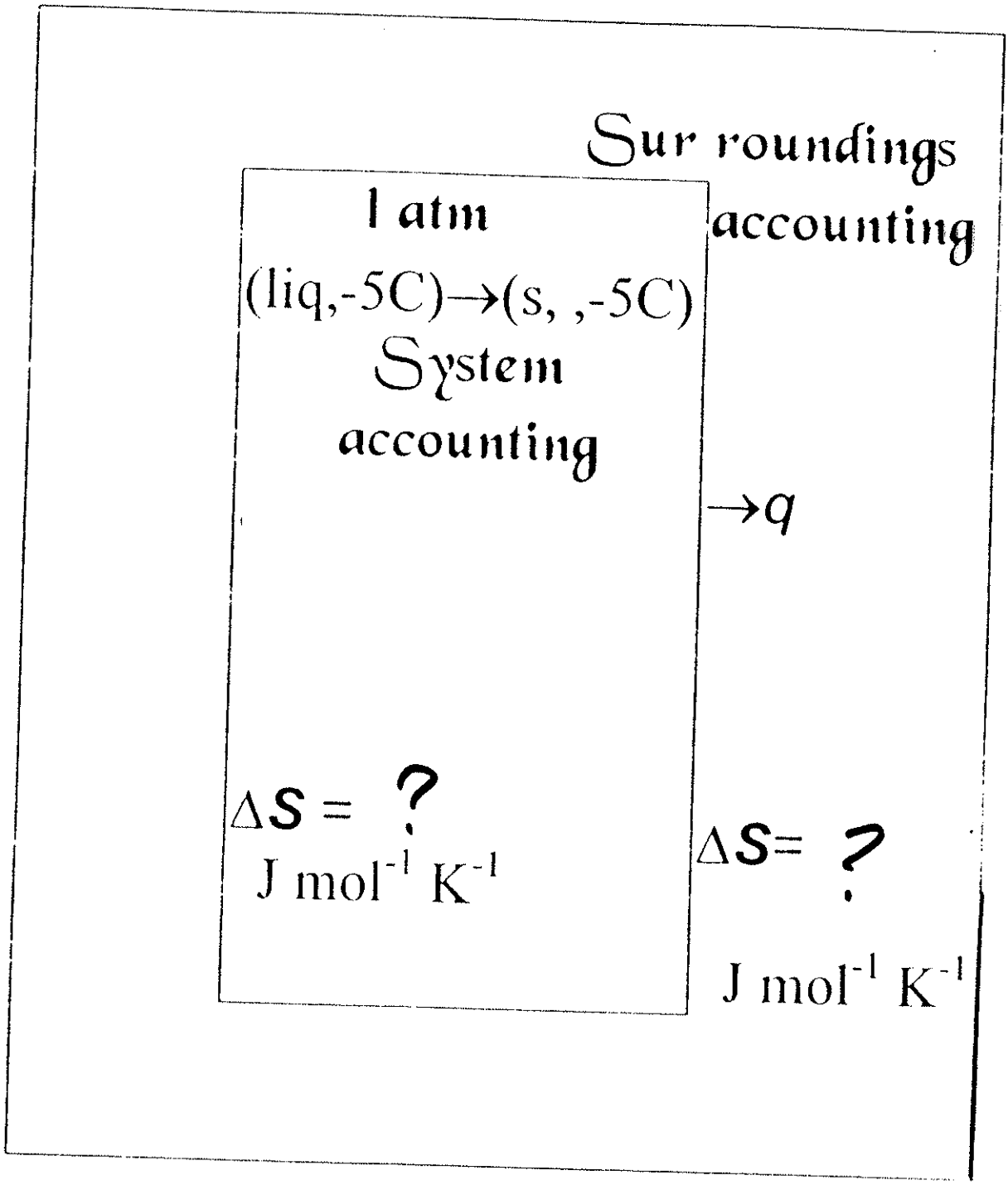


$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$

$= \quad ? \qquad J\ mol^{-1}\ K^{-1}$

spontaneous change ?

2.(a) The transition being considered is

liq at -5°C $\rightarrow$ solid at -5°C $\quad \Delta \boldsymbol{S}=?$

This is not a reversible process. In order to find $\Delta \boldsymbol{S}$ we need to imagine achieving this net result via a reversible process. Or, by constructing a cycle in which this step is a part of the cycle while the remaining steps in the cycle are carried out reversibly. Because entropy is a state function, $\Delta \boldsymbol{S}$ can be determined indirectly from the following cycle:

$$\begin{array}{ccc} & \overset{b}{} & \\ \text{liq at } 0°C & \leftarrow & \text{solid at } 0°C \\ c\downarrow & & \uparrow a \\ \text{liq at } -5°C & \rightarrow & \text{solid at } -5°C \\ & \underset{d}{} & \end{array}$$

Now $\Delta \boldsymbol{S}_{cycle} = 0$ since $\boldsymbol{S}$ is a state function. so

$0 = \Delta \boldsymbol{S}_a + \Delta \boldsymbol{S}_b + \Delta \boldsymbol{S}_c + \Delta \boldsymbol{S}_d$

Then solve for $\Delta \boldsymbol{S}_d$ which we want.

For the reversible heating and cooling, with no change in phase,

$\Delta \boldsymbol{S} = \int đq_{rev}/T = n \int C_p \, dT/T$

$\Delta \boldsymbol{S}_c = C_p(\text{liq}) \ln (268/273)$

$\Delta \boldsymbol{S}_a = C_p(\text{s}) \ln (273/268)$

For the reversible change in phase at that transition temperature at which the two phases are known to be in equilibrium at 1 atm:

$\Delta \boldsymbol{S} = \int đq_{rev}/T = q_p/T = \Delta_{trans}\boldsymbol{H} / T_{trans}$

solid at 0°C $\rightarrow$ liq at 0°C $\quad \Delta_{fus}\boldsymbol{H}$

$\Delta \boldsymbol{S}_b = \Delta_{fus}\boldsymbol{H} / 273$

Then, by difference,

$$\begin{aligned}
\Delta \boldsymbol{S}_d &= 0 - (\Delta \boldsymbol{S}_a + \Delta \boldsymbol{S}_b + \Delta \boldsymbol{S}_c) \\
&= - \{ C_p(\text{s}) \ln (273/268) \\
&\quad + \Delta_{fus}\boldsymbol{H}/273 + C_p(\text{liq}) \ln (268/273)\} \\
&= - [C_p(\text{liq}) - C_p(\text{s})] \ln (268/273) \\
&\qquad\qquad - \Delta_{fus}\boldsymbol{H}/273 \\
&= - 37.3 \ln (268/273) - 6010/273 \\
&= - 21.3 \text{ J K}^{-1} \text{ mol}^{-1}
\end{aligned}$$

For the surroundings, when the system changed:

liq at -5°C $\rightarrow$ solid at -5°C at 1 atm

the surroundings gained

$q = q_p = \Delta_{fus}\boldsymbol{H}_{268}$,

which is a number we do not have.

But since $\boldsymbol{H}$ is a state function, we can find $\Delta_{fus}\boldsymbol{H}_{268}$ from the same cycle:

For step a & c, $\Delta\boldsymbol{H} = \int C_p \, dT$ since $dp = 0$

For the cycle, $\Delta\boldsymbol{H} = 0$ for the system:

$$\Delta\boldsymbol{H}_{cycle} = 0 = \Delta\boldsymbol{H}_a + \Delta\boldsymbol{H}_b + \Delta\boldsymbol{H}_c + \Delta\boldsymbol{H}_d$$

$$0 = C_p(\text{s}) \, (273\text{-}268) + \Delta_{fus}\boldsymbol{H}_{273}$$

$$+C_p(\text{liq}) \, (268\text{-}273) - \Delta_{fus}\boldsymbol{H}_{268}$$

Then by difference, for the system,

$$\Delta_{fus}\boldsymbol{H}_{268} = -[C_p(\text{liq}) - C_p(\text{s})] \, (273\text{-}268) + \Delta_{fus}\boldsymbol{H}_{273}$$

$$= -37.3 \, (273\text{-}268) + 6010$$

$$= 5823.5 \text{ J mol}^{-1}$$

Thus, the surroundings gained

$q = 5823.5 \text{ J mol}^{-1}$

To find $\Delta S_{surroundings}$ we need to think of this amount of heat being transferred reversibly to the surroundings at 268 K

$\Delta S_{surroundings} = q_{rev}/T$

$= 5823.5 / 268 = +21.7 \text{ J K}^{-1} \text{ mol}^{-1}$

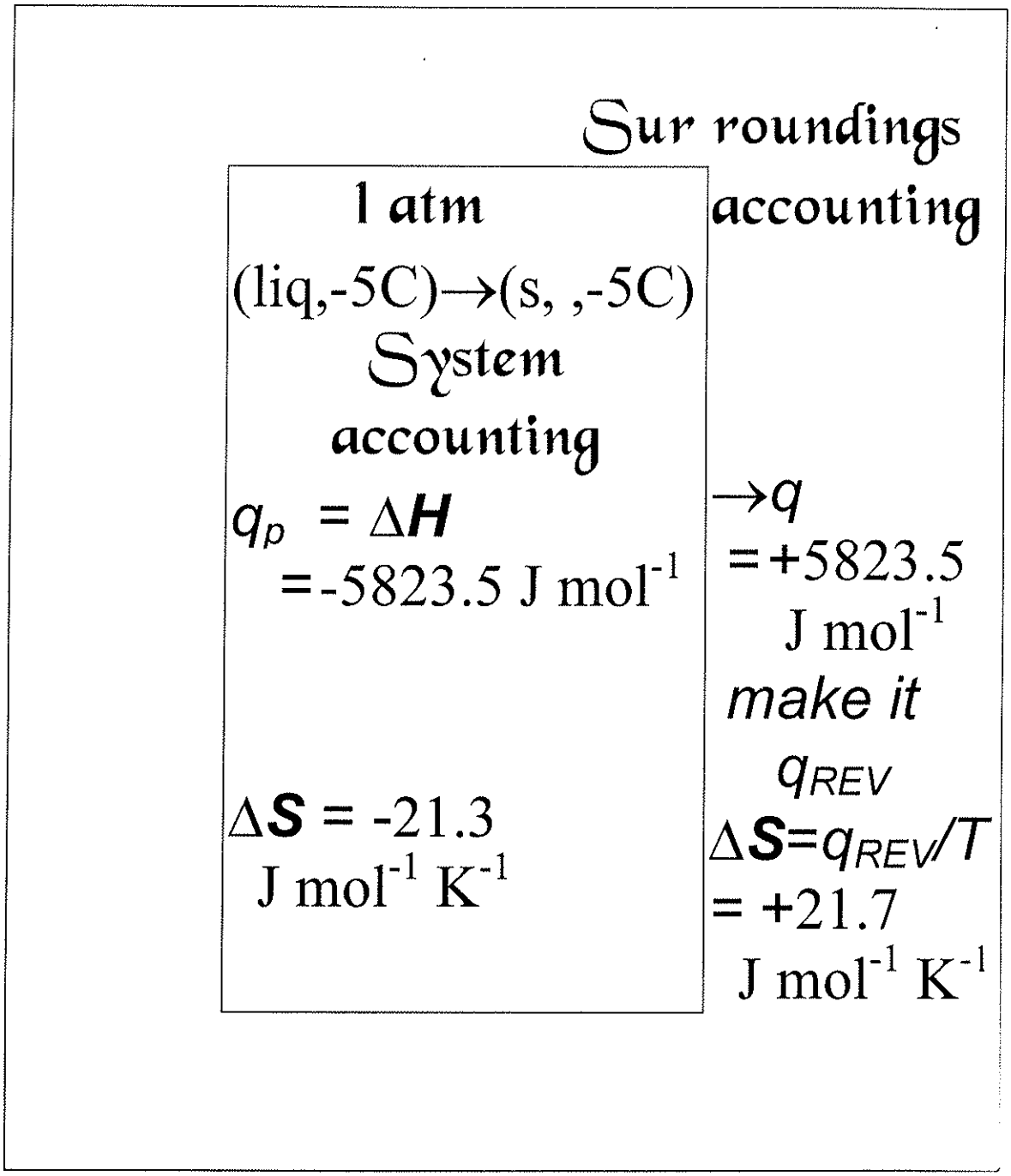
$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

$= -21.3 + 21.7 =$ ***positive***

Therefore the transformation of water

liq at -5°C $\rightarrow$ solid at -5°C

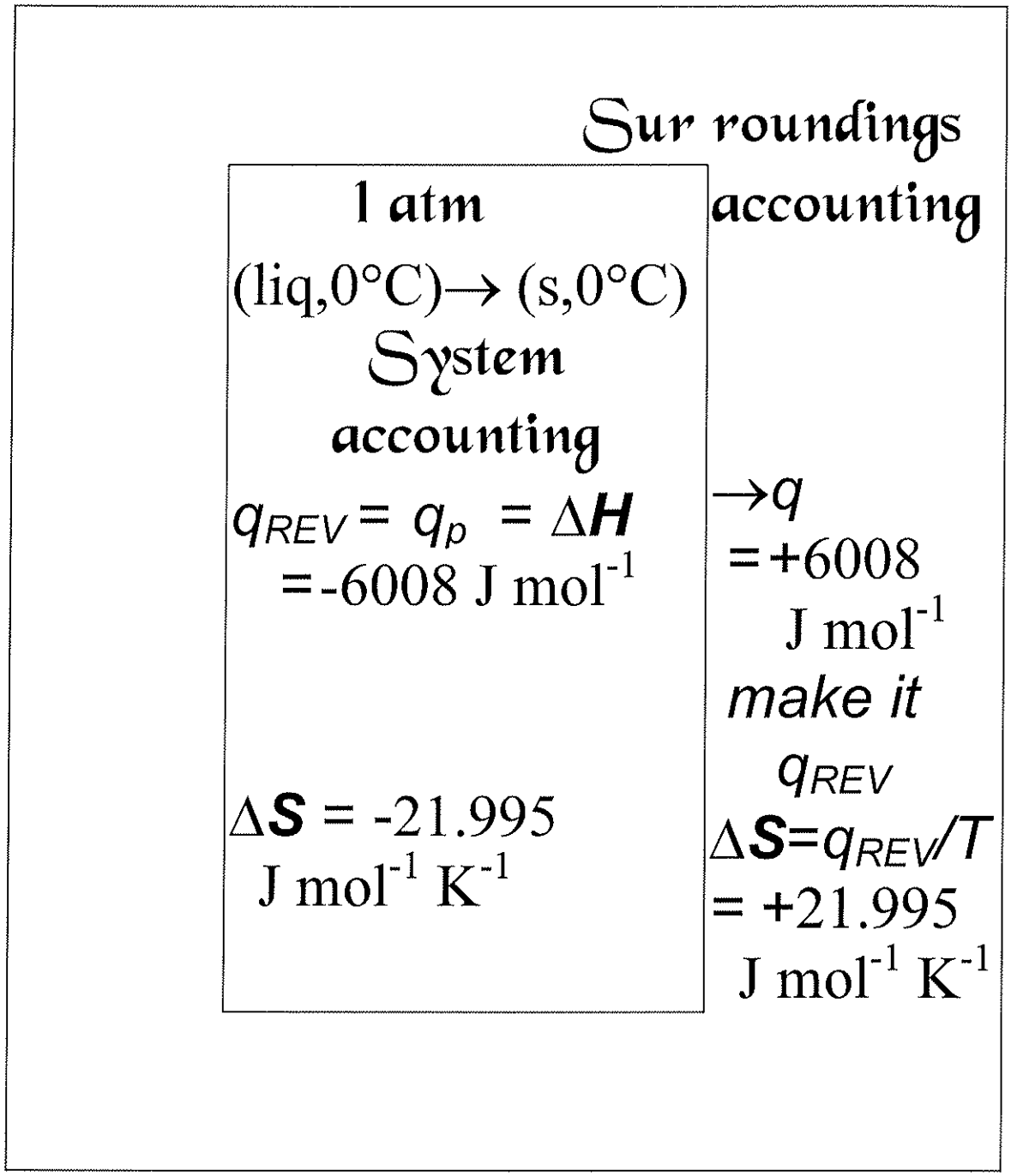
occurs <u>spontaneously</u>.



$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$
$$= -21.3 + 21.7 \text{ J mol}^{-1} \text{ K}^{-1} > 0$$

spontaneous change

IN CONTRAST:



$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

$$= -21.995 + 21.995 \text{ J mol}^{-1} \text{ K}^{-1} = 0$$

equilibrium

2.(b) The transition being considered is

liq at 95°C $\rightarrow$ gas at 95°C $\quad \Delta \boldsymbol{S}=?$

This is not a reversible process. In order to find $\Delta \boldsymbol{S}$ we need to imagine achieving this net result via a reversible process. Or, by constructing a cycle in which this step is a part of the cycle while the remaining steps in the cycle are carried out reversibly. Because entropy is a state function, $\Delta \boldsymbol{S}$ can be determined indirectly from the following cycle:

$$\begin{array}{ccc} & \overset{b}{} & \\ \text{liq at } 100°C & \leftarrow & \text{gas at } 100°C \\ c\downarrow & & \uparrow a \\ \text{liq at } 95°C & \rightarrow & \text{gas at } 95°C \\ & \underset{d}{} & \end{array}$$

Now $\Delta \boldsymbol{S}_{cycle} = 0$ since $\boldsymbol{S}$ is a state function.

$0 = \Delta \boldsymbol{S}_a + \Delta \boldsymbol{S}_b + \Delta \boldsymbol{S}_c + \Delta \boldsymbol{S}_d$

Then solve for $\Delta \boldsymbol{S}_d$ which we want.

For the reversible heating and cooling, with no change in phase,

$\Delta \boldsymbol{S} = \int đq_{rev}/T = n \int C_p \, dT/T$

$\Delta \boldsymbol{S}_c = C_p(\text{liq}) \ln (368/373)$

$\Delta \boldsymbol{S}_a = C_p(\text{g}) \ln (373/368)$

For the reversible change in phase at that transition temperature at which the two phases are known to be in equilibrium at 1 atm:

$\Delta \boldsymbol{S} = \int đq_{rev}/T = q_p /T = \Delta_{trans}\boldsymbol{H} / T_{\text{trans}}$

$\Delta \boldsymbol{S}_b = - \Delta_{vap}\boldsymbol{H} / 373$ (condensation)

Then, by difference,

$$\begin{aligned}
\Delta \boldsymbol{S}_d &= 0 - (\Delta \boldsymbol{S}_a + \Delta \boldsymbol{S}_b + \Delta \boldsymbol{S}_c) \\
&= - \{ C_p(\text{g}) \ln (373/368) - \Delta_{vap}\boldsymbol{H}/373 \\
&\qquad + C_p(\text{liq}) \ln (368/373)\} \\
&= - [C_p(\text{g}) - C_p(\text{liq})] \ln (373/368) \\
&\qquad + \Delta_{vap}\boldsymbol{H}/373 \\
&= + 41.9 \ln (373/368) + 40700/373 \\
&= +109.7 \text{ J K}^{-1} \text{ mol}^{-1}
\end{aligned}$$

For the surroundings, when the system changed:

liq at 95°C $\rightarrow$ gas at 95°C at 1 atm

the surroundings lost

$q = q_p = - \Delta_{vap}\boldsymbol{H}_{368}$

which is a number we do not have.

But since $\boldsymbol{H}$ is a state function, we can find $\Delta_{vap}\boldsymbol{H}_{368}$ from the same cycle:

For step a & c, $\Delta\boldsymbol{H} = \int C_p \, dT$ since $dp = 0$

For the cycle, $\Delta\boldsymbol{H} = 0$ for the system:

$$\Delta\boldsymbol{H}_{cycle} = 0 = \Delta\boldsymbol{H}_a + \Delta\boldsymbol{H}_b + \Delta\boldsymbol{H}_c + \Delta\boldsymbol{H}_d$$

$$0 = C_p(g)\,(373-368) - \Delta_{vap}\boldsymbol{H}_{373} + C_p(liq)\,(368-373) + \Delta_{vap}\boldsymbol{H}_{368}$$

Then by difference, for the system,

$$\Delta_{vap}\boldsymbol{H}_{368} = - [C_p(g) - C_p(liq)]\,(373-368) + \Delta_{vap}\boldsymbol{H}_{373}$$

$$= 41.9\,(373-368) + 40700$$

$$= 40.91 \text{ kJ mol}^{-1}$$

Thus, the surroundings lost

$q = - 40.91 \text{ kJ mol}^{-1}$

To find $\Delta \boldsymbol{S}_{\text{surroundings}}$ we need to think of this amount of heat being transferred reversibly to the surroundings at 368 K

$\Delta \boldsymbol{S}_{\text{surroundings}} = q_{rev}/T$

$= -40.91\times10^{3} / 368 = -111.2 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta \boldsymbol{S}_{\text{universe}} = \Delta \boldsymbol{S}_{\text{system}} + \Delta \boldsymbol{S}_{\text{surroundings}}$

$= 109.7 - 111.2 =$ ***negative***

Therefore the transformation of water

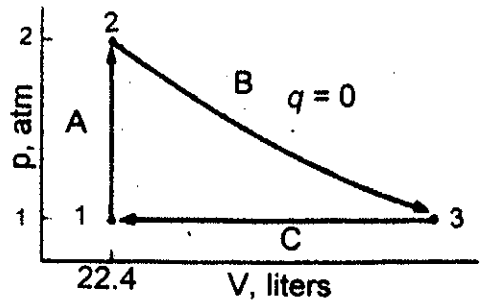
liq at 95°C $\rightarrow$ gas at 95°C

does not occur spontaneously, rather, the reverse transformation

gas at 95°C $\rightarrow$ liq at 95°C

occurs spontaneously.

3. One mole of a gas with $C_V = (3/2)R$ and equation of state $pV = RT + ap$ where $a = 0.020$ L mol^{-1} is put through the 3-step cycle Step A, Step B, Step C shown below.



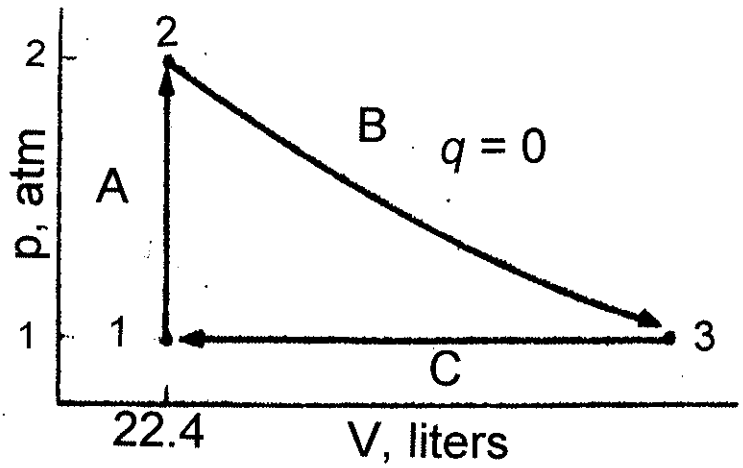
State	*p* *atm*	*V* *L*	*T* *K*
1	*1*	*22.4*	
2	*2*	*22.4*	
3	*1*		

Carry out the set-up and calculations and complete the information called for in the tables:

T_3 and V_3:

Step A	Step B	Step C
q	*q*	*q*
W	*W*	*W*
ΔU	ΔU	ΔU
ΔH	ΔH	ΔH
ΔS	ΔS	ΔS

EXAMPLE: **3.** One mole of a gas with $C_V = (3/2)R$ and equation of state $pV = RT + ap$ where $a = 0.020$ L mol^{-1} is put through the 3-step cycle Step A, Step B, Step C shown below.



State	*p* atm	*V* L	*T* K
1	*1*	*22.4*	
2	*2*	*22.4*	
3	*1*		

Carry out the set-up and calculations and complete the information called for in the tables:

Begin:

Use the equation of state $pV = RT + 0.02p$

State	*p* atm	*V* L	*T* K
1	*1*	*22.4*	***273***
2	*2*	*22.4*	***546***
3	*1*		

From $(1/T)\{\ p + (\partial \mathbf{U}/\partial V)_T\} = (\partial p/\partial T)_V$

$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$

From the equation of state

$pV = RT + ap$, we get $p = RT/(V-a)$

$(\partial p/\partial T)_V = R/(V-a) = p/T$

$\therefore (\partial \mathbf{U}/\partial V)_T = 0$ ♥

From $(1/T)\{-V + (\partial \mathbf{H}/\partial p)_T\} = -(\partial V/\partial T)_p$

$(\partial \mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V$

From the equation of state we get

$V = a + (RT/p)$

$(\partial \mathbf{H}/\partial p)_T = -(RT/p) + a + (RT/p)$

$\therefore (\partial \mathbf{H}/\partial p)_T = a$ ♥

From $C_p - C_V = \{\ p + (\partial U/\partial V)_T\}(\partial V/\partial T)_p$

From the equation of state $pV = RT + ap$

$(\partial V/\partial T)_p = R/p$

We had found already $(\partial \mathbf{U}/\partial V)_T = 0$ above

$\therefore\ C_p - C_V = p \times R/p = R$

Given $C_V = (3/2)R$

$\therefore C_p = (5/2)R$ ♥

To calculate T_3 and V_3 :

Step B (2→3) is an adiabatic ($q = 0$) <u>reversible</u> step, as figure shows.

$p_{op} = p$ $\quad$ $đW = -p_{op}dV = -pdV$

First law: $\Delta \boldsymbol{U} = q + W$, $\quad$ $d\boldsymbol{U} = đW$

$d\boldsymbol{U} = C_V dT + (\partial \boldsymbol{U}/\partial V)_T dV$

$d\boldsymbol{U} = C_V dT + (\partial \boldsymbol{U}/\partial V)_T dV = C_V dT + 0$

$d\boldsymbol{U} = đW = -pdV$

$\therefore C_V dT = -pdV$

$C_V dT = -[RT/(V-a)]\, dV$

$C_V dT/T = -R\, dV/(V-a)$

Integrating:

$C_V \ln(T_f/T_i) = -R \ln(V_f-a)/(V_i-a)$

$= R\ln(p_f T_i/p_i T_f)$ from $p = RT/(V-a)$

$C_V \ln(T_3/T_2) = R\ln(p_3 T_2/p_2 T_3)$

$= R \ln(p_3/p_2) + R \ln(T_2/T_3)$

$\therefore (C_V + R) \ln(T_3/T_2) = R \ln(p_3/p_2)$ ♥

$(5/2) \ln (T_3/546) = \ln(1/2)$ $\quad$ $\therefore T_3 = 414$ K

Eqn. of state: $V_3 - 0.020 = RT_3/p_3$

$\therefore V_3 = 34$ L

Now we can fill in this table

State	*p* *atm*	*V* *L*	*T* *K*
1	*1*	*22.4*	***273***
2	*2*	*22.4*	***546***
3	*1*	***34***	***414***

$d\boldsymbol{G} = -\boldsymbol{S}dT + Vdp$ $\quad$ $d\boldsymbol{A} = -\boldsymbol{S}dT - pdV$

Since none of the steps are $dT = 0$, we can not calculate $\Delta\boldsymbol{G}$ or $\Delta\boldsymbol{A}$ without having $\boldsymbol{S}$ itself for this gas.

Step A	Step B	Step C
$dV=0$	adiabatic, $q=0$ & reversible	$dp = 0$
$q_V = \Delta \boldsymbol{U}$ get from below	$q = 0$ given	$q_p = \Delta \boldsymbol{H}$ get from below
$W = -\int p_{op} dV$ $W = 0$ since $dV = 0$	$W = \Delta \boldsymbol{U}$ get from below	$W = -\int p_{op} dV$ $= -p_{op} \int dV$ $= -1 \int dV$ $= -1(22.4-34)$ L atm
$\Delta \boldsymbol{U}$ $d\boldsymbol{U} = C_V dT$ $+(\partial \boldsymbol{U}/\partial V)_T dV$ $= C_V dT + 0$ $\Delta \boldsymbol{U} = \int C_V dT =$ $(3/2)(8.3144)$ $\times(546-273)$ J	$\Delta \boldsymbol{U}$ same here $\Delta \boldsymbol{U} = \int C_V dT =$ $(3/2)(8.3144)$ $\times(414-546)$ J	$\Delta \boldsymbol{U}$ same here $\Delta \boldsymbol{U} = \int C_V dT =$ $(3/2)(8.3144)$ $\times(273-414)$ J

$$d\boldsymbol{H} = C_p dT + (\partial \boldsymbol{H}/\partial p)_T dp$$
$$= C_p dT + a dp$$
$$\Delta \boldsymbol{H} = \int C_p dT + \int a dp \quad \heartsuit$$

$\Delta \boldsymbol{H}$	$\Delta \boldsymbol{H}$	$\Delta \boldsymbol{H}$
$=$	$=$	$=$
$(5/2)(8.3144)$	$(5/2)(8.3144)$	$(5/2)(8.3144)$
$\times(T_2 - T_1)$	$\times(T_3 - T_2)$	$\times(T_1 - T_3)$
$+0.02\ \text{L mol}^{-1}$	$+0.02\ \text{L mol}^{-1}$	$+0\ (dp=0)$
$\times(p_2 - p_1)$	$\times(p_3 - p_2)$	$=$
$=$	$=$	$(5/2)(8.3144)$
$(5/2)(8.3144)$	$(5/2)(8.3144)$	$\times(273-414)$
$\times(546-273)$	$\times(414-546)$	J
$+ 0.02\times(2-1)$	$+ 0.02\times(1-2)$	
$\times(8.3144/$	$\times(8.3144/$	
$0.082056)$ J	$0.082056)$ J	

$d\boldsymbol{S} = C_V dT/T + (\partial \boldsymbol{S}/\partial V)_T dV$

but $(\partial \boldsymbol{S}/\partial V)_T = (\partial p/\partial T)_V = R/(V-a)$

$d\boldsymbol{S} = C_V dT/T + R\,dV/(V-a)$ ♥

or $d\boldsymbol{S} = C_p dT/T + (\partial \boldsymbol{S}/\partial p)_T dp$

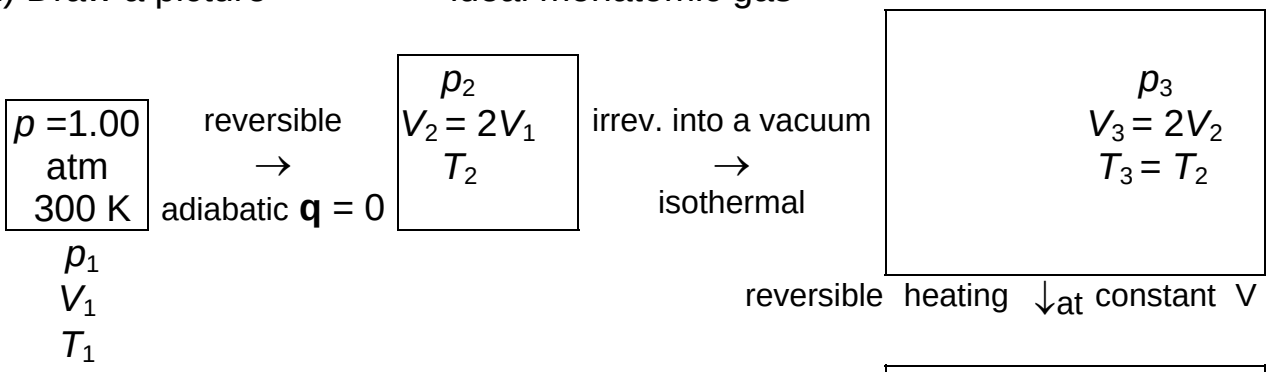
but $(\partial \boldsymbol{S}/\partial p)_T = -(\partial V/\partial T)_p = -R/p$

$d\boldsymbol{S} = C_p dT/T - R dp/p$ ♥

$\Delta \boldsymbol{S}$ for $dV = 0$	$\Delta \boldsymbol{S}$	$\Delta \boldsymbol{S}$ for $dp = 0$
$d\boldsymbol{S} = C_V dT/T$	$đq_{rev} = 0$	$d\boldsymbol{S} = C_p dT/T$
$\Delta \boldsymbol{S} = \int C_V dT/T$	$\therefore \Delta \boldsymbol{S} = 0$	$\Delta \boldsymbol{S} = \int C_p dT/T$
=	or	=
(3/2)(8.3144)	$d\boldsymbol{S} = C_p dT/T$	(5/2)(8.3144)
ln(546/273)	$- R dp/p$	ln(273/414)
J K^{-1}	$\Delta \boldsymbol{S} = \int C_p dT/T$	J K^{-1}
	$- R \int dp/p$	
	=	
	(5/2)(8.3144)	
	ln(414/546)	
	- 8.3144	
	ln(2/1) = 0	

Problem: Two moles of a monatomic ideal gas begins in a state with p = 1.00 atm and T = 300 K. It is expanded reversibly and adiabatically until the volume has doubled; then it is expanded irreversibly and isothermally into a vacuum until the volume has doubled again; then it is heated reversibly and isothermally until a final state with p = 1.00 atm and T = 400 K is reached. Calculate $\Delta \boldsymbol{S}$ system for this process. (Hint: There is an easy way to solve this problem and a hard way. You should, of course, choose the easy way.)

(1) Draw a picture ideal monatomic gas



initial final

(2) Recall the definitions of concepts and terms:

Second law of thermodynamics, $d\boldsymbol{S} = d\mathbf{q}_{rev}/T$

definition of heat capacity: $dq = C\, dT$

heat capacities of one mole of an ideal gas are related: $C_p = C_V + R$

heat capacity at constant volume for a monatomic gas is entirely due to its translational energy

kinetic energy $= 3/2 k_B T$ for one molecule $N_{Avogadro} \times k_B = R$

Sum up over all the infinitesimal slivers $d\boldsymbol{S}$ to get:

$\int_{Si}^{Sf} d\boldsymbol{S} = \boldsymbol{S}_f - \boldsymbol{S}_i = \Delta\boldsymbol{S}$ because $\boldsymbol{S}$ is a state function.

(3) Solve the problem in the space below:

Using the concept that $\boldsymbol{S}$ *is a state function*, we could go from the given initial state to the given final state via a reversible one-step constant pressure heating, for which path:

p =1.00 atm 300 K	constant p reversible → heating $d\mathbf{q}_{rev} = C_p\, dT$	p =1.00 atm 400 K

$\int_{Si}^{Sf} d\boldsymbol{S} = \boldsymbol{S}_f - \boldsymbol{S}_i = \Delta\boldsymbol{S} = \int_{Ti}^{Tf} d\mathbf{q}_{rev}/T = \int_{Ti}^{Tf} C_p\, dT / T = C_p \ln(T_f / T_i)$

Since this is a monatomic gas, $C_V = 3/2R$.

Since it is an ideal gas, $C_p = C_V + R = (5/2)R$

$C_p = (5/2)(8.31451\ J\ K^{-1}\ mol^{-1})$

$\Delta\boldsymbol{S} = C_p \ln(T_f / T_i) = 2\ mol \times (5/2)(8.31451\ J\ K^{-1}\ mol^{-1}) \times \ln(400/300)$

$\Delta\boldsymbol{S}_{system} =$ 11.96 $J\ K^{-1}$

Alternatively we could have solved the problem by calculating $\Delta\boldsymbol{S}$ for each step and adding up the values to get the overall $\Delta\boldsymbol{S}$.

Considering each step separately:

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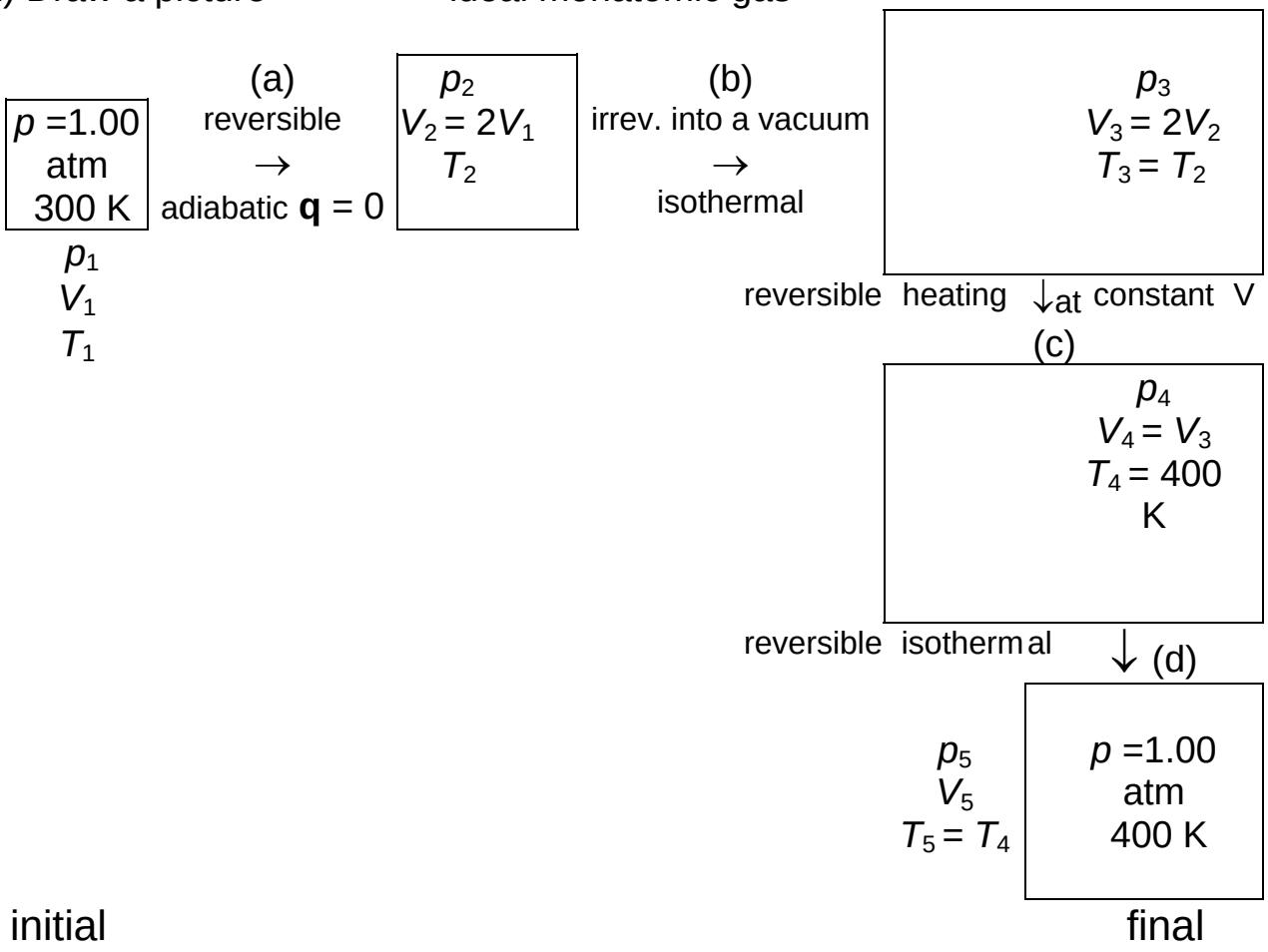
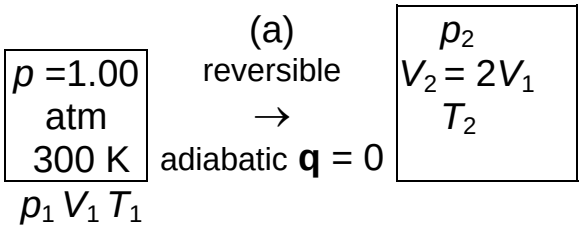
(1) Draw a picture ideal monatomic gas



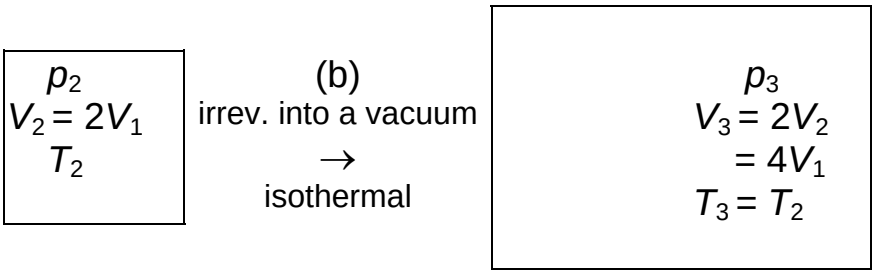
Let us examine each step; if we had to calculate $\Delta \boldsymbol{S}_{\text{system}}$ for just this step, how would we do it? In the following pages we analyze <u>what do we know about each step</u> ? <u>based on what concept</u> or known condition of the system before/after for each step? to see how to go about calculating various quantities like C_V , C_p , **q**, $\boldsymbol{w}$, $\Delta \boldsymbol{U}$., $\Delta \boldsymbol{S}$, for an ideal gas.



Since this was a reversible step, $d\mathbf{q}_{rev} = d\mathbf{q} = 0$, $\therefore d\boldsymbol{S}_{system} = 0$ for this step
Also, we can find out all the other quantities, including the $p\ V$ and T for state 2, which we shall need in order to get the description of state 3.

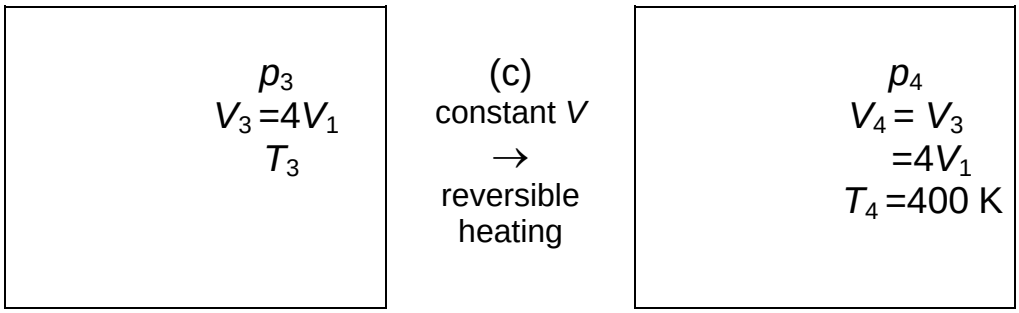
	What do we know?	Based on what concept?
1	$\Delta\boldsymbol{U} = \mathbf{q}+\mathbf{w}$	First law of thermodynamics
2	$\mathbf{q} = 0$	definition of adiabatic
3	$d\boldsymbol{U} = C_V\ dT$	ideal gas, internal energy depends only on temperature
4	$C_V = (3/2)$R per mole	monatomic gas
5	$d\mathbf{w} = -\ p_{opposing}\ dV$	definition of work
6	$p_{gas} = p_{opposing}$ at all times	reversible
7	$p_{gas}\ V = nRT$	ideal gas
8	$d\boldsymbol{S} = d\mathbf{q}_{rev}\ /T$	Second law of thermodynamics
9	$\therefore d\boldsymbol{U} = d\mathbf{w}$	1 & 2
10	$d\mathbf{w} = -\ (nRT/V)\ dV$	5, 6 & 7
11	$d\boldsymbol{U} = n(3/2)R\ dT$	3 & 4
12	$\therefore n(3/2)R\ dT = -\ (nRT/V)\ dV$	9, 10 & 11
13	$(3/2)\ dT\ /T = -\ dV\ /\ V$	rearrange
14	$(3/2)\ \ln(T_2\ /T_1) = -\ \ln(V_2\ /\ V_1)$	summing up on both sides
15	$\Delta\boldsymbol{U}_a = n(3/2)$R $(T_2\ -T_1)$	summing up the small $d\boldsymbol{U}$ in 11
16	$\therefore \mathbf{w} = \Delta\boldsymbol{U}$	9
17	$\mathbf{q} = \mathbf{q}_{rev}$	reversible
18	$\therefore d\boldsymbol{S} = 0$	2, 8, 17
19	$\therefore \Delta\boldsymbol{S}_a = 0$	summing up the small $d\boldsymbol{S}$ in 18

we are given p_1, T_1 and n ,
so we can solve for V_1 from $p_1\ V_1 = n\ RT_1$
we are given $V_2 = 2V_1$, which when substituted into eq. 14 gives
$(3/2)\ \ln(T_2\ /T_1) = -\ \ln(V_2\ /\ V_1) = -\ln(2)$ or $(T_2\ /300)^{3/2} = (1/2)$
Now that we have V_2, and T_2, we can calculate all the quantities: Calculate $\Delta\boldsymbol{U}$ from 15. Calculate **w** from 16. Calculate p_2 from 7.

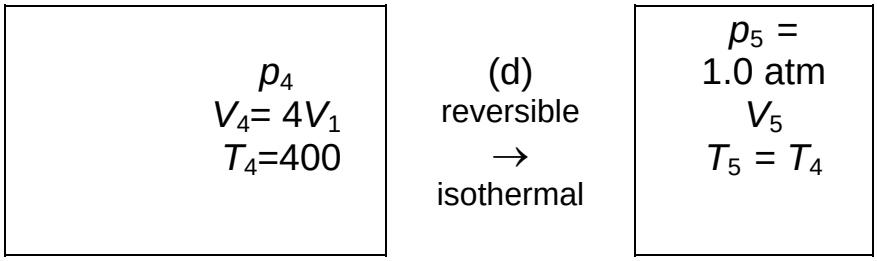


	What do we know?	Based on what concept?
1	$\Delta \boldsymbol{U} = \mathbf{q}+\mathbf{w}$	First law of thermodynamics
2	$\mathrm{d}T = 0$	isothermal
3	$\mathrm{d}\boldsymbol{U} = C_V\ \mathrm{d}T$	ideal gas, internal energy depends only on temperature
4	$C_V = (3/2)\mathrm{R}$ per mole	monatomic gas
5	$\mathrm{d}\mathbf{w} = -\ p_{\text{opposing}}\ \mathrm{d}V$	definition of work
6	$p_{gas}\ V = nRT$	ideal gas
7	$\mathrm{d}\boldsymbol{S} = \mathrm{d}\mathbf{q}_{\text{rev}}\ /T$	Second law of thermodynamics
8	$p_2V_2 = nRT_2$	ideal gas in state 2
9	$p_3 2V_2 = nRT_2$	ideal gas in state 3, $T_3=T_2$, $V_3=2V_2$
10	$\therefore\ p_3 = ½\ p_2$	9 ÷ 8
11	$p_{\text{opposing}} = 0$	expansion into vacuum
12	$\therefore\ \mathbf{w} = 0 = \mathbf{w}_{\text{irrev}}$	5 & 11, expansion into vacuum is irrev
13	$\therefore\ \mathbf{q} = \mathbf{q}_{\text{irrev}} = \Delta \boldsymbol{U}$	1 & 12
14	$\mathrm{d}\boldsymbol{U} = n(3/2)R\ \mathrm{d}T$	3 & 4
15	$\Delta \boldsymbol{U} = n(3/2)\mathrm{R}\ (T_3 - T_2)$	summing up the small $\mathrm{d}\boldsymbol{U}$ in 14
16	$\therefore\ \Delta \boldsymbol{U}_{\text{b}} = 0$	2 & 15
17	$\mathbf{q}_{\text{irrev}} = 0$	13 & 16
18	we need $\mathbf{q}_{\text{rev}} = -\ \mathbf{w}_{\text{rev}}$	1 & 16
19	$p_{\text{gas}} = p_{\text{opposing}}$ at all times	imagine a reversible expansion
20	$\mathrm{d}\mathbf{w}_{\text{rev}} = -\ (nRT/V)\ \mathrm{d}V$	5, 6 & 19
21	$\mathbf{w}_{\text{rev}} = -\ nRT_2\ \ln\ (2V_2\ /V_2)$	summing up the small $\mathrm{d}\mathbf{w}$ in 20
22	$\therefore\ \mathbf{q}_{\text{rev}} = +nRT_2\ \ln\ (2V_2\ /V_2)$	18 & 21
23	$\therefore\ \Delta \boldsymbol{S}_{\text{b}} = nR\ \ln\ (2)$	7 & 22

Now we know $p_3 = ½\ p_2$, $V_3 = 2V_2 = 4V_1$, $T_3 = T_2$.



	What do we know?	Based on what concept?
1	$\Delta \boldsymbol{U} = \mathbf{q}+\mathbf{w}$	First law of thermodynamics
2	$dV = 0$	constant volume
3	$d\boldsymbol{U} = C_V\ dT$	ideal gas, internal energy depends only on temperature
4	$C_V = (3/2)$R per mole	monatomic gas
5	$d\mathbf{w} = -\ p_{\text{opposing}}\ dV$	definition of work
6	$p_{gas}\ V = nRT$	ideal gas
7	$d\boldsymbol{S} = d\mathbf{q}_{\text{rev}}\ /T$	Second law of thermodynamics
8	$\mathbf{w} = 0$	2 & 5
9	$\therefore\ d\boldsymbol{U} = d\mathbf{q}$	1 & 8
10	$d\boldsymbol{U} = n(3/2)R\ dT$	3 & 4
11	$d\mathbf{q} = d\mathbf{q}_{\text{rev}}$	reversible heating
12	$\therefore\ d\mathbf{q}_{\text{rev}} = n(3/2)R\ dT$	9, 10, & 11
13	$\therefore\ d\boldsymbol{S} = n(3/2)R\ dT/T$	7, 12
14	$\therefore\ \Delta\boldsymbol{S}_c = n(3/2)R \ln(T_4/T_3)$	summing up the small $d\boldsymbol{S}$ in 13
15	$\therefore\ \Delta\boldsymbol{U}_c = n(3/2)\text{R}\ (T_4 - T_3)$	summing up the small $d\boldsymbol{U}$ in 10
16	$\therefore\ \mathbf{q}_{\text{rev}} = n(3/2)\text{R}\ (T_4 - T_3)$	9 & 15
17	$p_4 = nRT_4 / V_3$	2 & 6
18	$p_4 = nR400/4\ V_1$	$V_4 = V_3 = 2V_2 = 4V_1$, $T_4 = 400$
19	$\Delta\boldsymbol{S}_c = n(3/2)R \ln(400/T_2)$	$(T_4/T_3) = (400\text{ K}/T_2)$
20	$\Delta\boldsymbol{S}_c = n(3/2)R \ln(400/300) + nR \ln(2)$	19 and $(T_2/300)^{3/2} = (1/2)$ from step (a)



	What do we know?	Based on what concept?
1	$\Delta \boldsymbol{U} = \mathbf{q} + \mathbf{w}$	First law of thermodynamics
2	$dT = 0$	isothermal
3	$d\boldsymbol{U} = C_V\ dT$	ideal gas, internal energy depends only on temperature
4	$C_V = (3/2)$R per mole	monatomic gas
5	$d\mathbf{w} = -\ p_{\text{opposing}}\ dV$	definition of work
6	$p_{gas}\ V = nRT$	ideal gas
7	$d\boldsymbol{S} = d\mathbf{q}_{\text{rev}}\ /T$	Second law of thermodynamics
8	$p_{\text{gas}} = p_{\text{opposing}}$ at all times	reversible
9	$p_4 V_4 = nRT_4$	ideal gas in state 4
10	$p_5 V_5 = nRT_5$; $V_5 = nR400\ \text{K}/1\ \text{atm})$	ideal gas in state 5
11	$V_5 = V_4\ (p_4/1\ \text{atm})$	10 ÷ 9
12	$V_5\ /V_4 = 400/(300\times4) = 1/3$	11, $p_4 = nR\ 400\ \text{K}/4\ V_1$ step (c) and 1 atm = nR300 / V_1 step (a)
13	$d\mathbf{w}_{\text{rev}} = -\ (nRT/V)\ dV$	5, 6 & 8
14	$d\boldsymbol{U} = 0$	2 & 3
15	$\therefore\ d\mathbf{q}_{\text{rev}} = -\ d\mathbf{w}_{\text{rev}}$	1 & 14
16	$\therefore\ d\mathbf{q}_{\text{rev}} = (nRT/V)\ dV$	13 & 15
17	$d\boldsymbol{S} = nR\ dV/V$	7 & 16
18	$\Delta \boldsymbol{S}_{\text{d}} = nR\ \ln(V_5/V_4)$ $= nR\ \ln(1/3)$	summing up the small $d\boldsymbol{S}$ in 17 and 12
19	$\mathbf{w}_{\text{rev}} = -\ nRT_4 \ln(V_5/V_4)$ $= -\ nR\ 400\ \ln(1/3)$	summing up the small $d\mathbf{w}$ in 13 and 12
20	$\mathbf{q}_{\text{rev}} = nR\ 400\ \ln(1/3)$	15 & 19

Now we know everything about each and every step.

Summary: $\Delta \boldsymbol{S}_{total} = \Delta \boldsymbol{S}_a + \Delta \boldsymbol{S}_b + \Delta \boldsymbol{S}_c + \Delta \boldsymbol{S}_d$

(a)	$\Delta \boldsymbol{S}_a = 0$
(b)	$\Delta \boldsymbol{S}_b = nR \ln (2)$
(c)	$\Delta \boldsymbol{S}_c = n(3/2)R \ln(400/300) + nR \ln(2)$
(d)	$\Delta \boldsymbol{S}_d = nR \ln(1/3)$
all	$\Delta \boldsymbol{S}_{total} = nR \ln[(4/3)(400/300)^{3/2}]$ $= nR\ (5/2) \ln\ (400/300)$
	$\therefore\ \Delta \boldsymbol{S}_{total} = 11.96\ \text{J K}^{-1}$

exactly the same answer as was obtained doing it the easy way

Summary: $\Delta \boldsymbol{U}_{total} = \Delta \boldsymbol{U}_a + \Delta \boldsymbol{U}_b + \Delta \boldsymbol{U}_c + \Delta \boldsymbol{U}_d$

(a)	$\Delta \boldsymbol{U}_a = n(3/2)R\ (T_2 - T_1)$
(b)	$\Delta \boldsymbol{U}_b = 0$
(c)	$\Delta \boldsymbol{U}_c = n(3/2)R\ (T_4 - T_3)$
(d)	$\Delta \boldsymbol{U}_d = 0$
all	$\Delta \boldsymbol{U}_{total} = n(3/2)R\ (T_2 - T_1 + T_4 - T_3)$ $= n(3/2)R\ (T_4 - T_1)$
	$\therefore\ \Delta \boldsymbol{U}_{total} = 2494.35\ \text{J}$

since $(T_2 = T_3)$

exactly the same answer as can be obtained by going directly from initial to final state, using $\Delta \boldsymbol{U} = n(3/2)R\ (T_f - T_i)$

Summary:

$\mathbf{q}_{total} = \mathbf{q}_a + \mathbf{q}_b + \mathbf{q}_c + \mathbf{q}_d$ $\qquad$ $\boldsymbol{w}_{total} = \boldsymbol{w}_a + \boldsymbol{w}_b + \boldsymbol{w}_c + \boldsymbol{w}_d$

(a)	$\mathbf{q}_a = 0$	$\mathbf{w} = n(3/2)R\ (T_2 - T_1)$
(b)	$\mathbf{q}_{irrev} = 0$	$\mathbf{w}_{irrev} = 0$
(c)	$\mathbf{q}_{rev} = n(3/2)R\ (T_4 - T_3)$	$\mathbf{w} = 0$
(d)	$\mathbf{q}_{rev} = nR\ 400 \ln(1/3)$	$\mathbf{w}_{rev} = -\ nR\ 400 \ln(1/3)$
all	$\mathbf{q}_{total} = n(3/2)R(T_4 - T_3)$ $+\ nR\ 400 \ln(1/3)$	$\boldsymbol{w}_{total} = n(3/2)R(T_2 - T_1)$ $-\ nR\ 400 \ln(1/3)$
	$\Delta \boldsymbol{U}_{total} = \mathbf{q}_{total} + \boldsymbol{w}_{total}$ $= n(3/2)R\ (T_2 - T_1 + T_4 - T_3)$ $= 2494.35\ \text{J}$	exactly the same answer as above