Problem 1.   TA Session

20-5. In this problem, we will prove that Equation 20.5 is valid for an arbitrary system. To do this, consider an isolated system made up of two equilibrium subsystems, A and B, which are in thermal contact with each other; in other words, they can exchange energy as heat between themselves. Let subsystem A be an ideal gas and let subsystem B be arbitrary. Suppose now that an infinitesimal reversible process occurs in A accompanied by an exchange of energy as heat δq_{rev}(ideal). Simultaneously, another infinitesimal reversible process takes place in B accompanied by an exchange of energy as heat δq_{rev}(arbitrary). Because the composite system is isolated, the First Law requires that

$$\delta q_{rev}(\text{ideal}) = -\delta q_{rev}(\text{arbitrary})$$

Now use Equation 20.4 to prove that

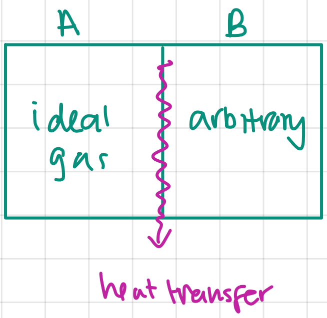
$$\oint \frac{\delta q_{rev}(\text{arbitrary})}{T} = 0$$

Therefore, we can say that the definition given by Equation 20.4 holds for any system.

Equation 20.5 → $\int \frac{\delta q_{rev}}{T} = \emptyset$ infinitesimal reversible process } both A & B
pg 821   exchange of δq_{rev}

$\delta q_{rev}(\text{ideal}) = -\delta q_{rev}(\text{arbitrary})$

$\delta q_{rev}(A) = -\delta q_{rev}(B)$



show $\oint \frac{\delta q_r(\text{arbitrary})}{T} = \emptyset$

from first law we derive

use eq 20.1 → $\delta q_{rev} = dU - \delta w_{rev} = C_V(T)\,dT + P\,dV$

$= C_V(T)\,dT + \frac{nRT}{V}\,dV$

$\therefore\ \delta q_{rev}(B) = \underbrace{-\left(C_V(T)\,dT + \frac{nRT}{V}\,dV\right)}_{q_{rev}(A)}$

$\frac{\delta q_{rev}(B)}{T} = -\frac{C_V}{T}\,dT + \frac{nR\cancel{T}}{\cancel{T}V}\,dV$

$= d\left[\int -\frac{C_V(T)}{T}\,dT - nR\int \frac{dV}{V} + C\right]$

* Cyclic integral of state function $= \emptyset$

$$\oint dY = \emptyset$$

$$\oint dY = \int_1^2 dY + \int_2^1 dY = Y_2 - Y_1 + (Y_1 - Y_2) = \emptyset$$

therefore: $\oint \frac{\delta q_{rev}\,(arbitrary)}{T} = \emptyset$

Problem #2

Calculate ΔH & ΔS for system & surrounding when 1 mol of water is vaporized at 100 °C. Value of $\Delta H_{vap} = 40.65$ kJ/mol. Comment on sign of $\Delta \bar{S}^\circ_{vap}$

at const. pressure, $\Delta H = \Delta U + \Delta(PV)$

$\Delta U = q + w = q - P\Delta V$

so, $\Delta H = q - \cancel{P\Delta V} + \overset{\text{bc constant}}{\cancel{P\Delta V}}$

so, $\Delta H = q$ at constant Pressure

$\Delta H_{sys} = \Delta H_{vap}$

$\Delta H_{sys} = -\Delta H_{surr}$

$\Delta S = \frac{\delta q_{rev}}{T}$ where $\Delta H = q$

so, $\Delta S = \frac{\Delta H_{sys}}{T}$

* convert to Kelvin

and $\Delta S_{sys} = -\Delta S_{surr}$

ProbUm #3

Calculate ΔS of system and surr when 1mol of ideal monoatomic gas doubles in volume.

a) isothermal reversible expansion   page 822

$\Delta T = \emptyset$
$\Delta U = \emptyset$

$$\Delta S = \int \frac{q_{rev}}{T_1} \Rightarrow \int_{V_1}^{V_2} \frac{1}{T_1} \frac{nRT_1}{V} dV \Rightarrow nR \int_{V_1}^{V_2} \frac{dV}{V}$$

I got this from book

$$\Delta S = nR \ln\left(\frac{2V}{V}\right)$$

$$\Delta S_{system} = -\Delta S_{surr}$$

b) isothermal, irreversal, in vaccum

$\Delta T = \emptyset$
$\Delta U = \emptyset$

$P_{ex} = \emptyset$
$W = \emptyset$

$$\Delta S_{surr} = \frac{q_{surr}}{T} = -\frac{q_{sys}^{actual}}{T}$$

$$^{irrev}\Delta S_{system} = {}^{rev}\Delta S_{system} = nR\ln\left(\frac{2V}{V}\right)$$

$\Delta S_{surr} = \dfrac{q_{surr}}{T}$ where $\Delta U = q_{surr} + w$
$\emptyset = q_{surr} + \emptyset$
$q_{surr} = \emptyset$

so, $\Delta S_{surr} = \emptyset$

In vacuum means $\Delta S_{surr} = \emptyset$

c) adiabatic reversible expansion

$\Delta q = 0$ $\quad \Delta S = \frac{q_{rev}}{T}$ $\quad \Delta S_{system} = -\Delta S_{surr}$

d) adiabatic irreversible expansion into a vacuum

$\Delta q = 0$ * from notes, since ΔS is a state function, we change the system to make it reversible, so we can use $\Delta S = \frac{q_{rev}}{T}$
because $\Delta U = 0$, we use isothermal reversible

$P_{ext} = 0$
$w = 0$

$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$ where $\frac{2V}{V}$

Problem 4

1mol ideal gas
$T_{sys} = 300K$ isothermal until $P = P_{ext}$ (irreversible)
$V_1 = 25L$ $\quad V_f = 10L$
$T_{surr} = 300K$ $\quad$ find S_{sys}, S_{surr}, S_{univ}

isothermal, irreversible
$\Delta T = 0$ $\quad$ ↳ ΔS is state function so we can use $\Delta S_{sys} = nR\ln\left(\frac{V_2}{V_1}\right)$

$P_{ext} = P_f$ where $\delta q_{sys} = \delta w = -P_f \Delta V$

*in this case $\Delta S \neq 0$ and $\Delta S_{surr} \neq \Delta S_{sys}$

$P_f = \frac{nRT_f}{V_f}$ then, $w = -P_f\left(\frac{V_f}{V_i}\right)$

and $q = -w$ and $\Delta S = \frac{-\delta q_{surr}}{T}$

and $S_{univ} = S_{sys} + S_{sur}$

find P_f to find w to find q to find S_{surr} where $P_f = P_{ext}$ using ideal gas law

Problem 5

2.5mol ideal monoatomic gas
$T_1 = 310K$ $\quad P_1 = 1\text{ bar}$
calculate q, w, ΔU, ΔH, ΔS

can use $\Delta S_{sys} = -\Delta S_{surr}$ as long as $q \neq 0$
$S_{surr} = 0$ when adiabatic
for prob 5,

a) gas heated to 675K and constant $P_{ext} = 1$ bar

First, find V_1, use $PV = nRT \Rightarrow V_1 = \frac{nRT_1}{P_1}$ * constant pressure

then, using Charle's law: at $\Delta P = \emptyset$, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

so $V_2 = V_1 \cdot \frac{T_2}{T_1}$ then $w = -P_{ext}\Delta V$

$\Delta U = \frac{3}{2} nRT$

at constant pressure $\rightarrow$ $q = \Delta H = \underbrace{\Delta U + P\Delta V}_{(\Delta U - w)}$

and since $q = C_v nR\Delta T$, $\Delta S = \frac{\delta q_{rev}}{T} = \int \frac{C_v(T)}{T} dT + \int \frac{nR}{V} dv$

$= \frac{3}{2} nR \ln \frac{T_f}{T_i} + \frac{3}{2} nR \ln\left(\frac{V_f}{V_i}\right)$

b) $T_2 = 675K$ at constant volume, $V_i = V_f$
$\downarrow$
$w = \emptyset$

$\frac{PV}{V} = \frac{nRT}{V}$

$\Delta U = q + \cancel{w}^{0}$

$q = \Delta U = \frac{3}{2} nR\Delta T$

$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta\left(\frac{nRT}{\cancel{V}} \cdot \cancel{V}\right) = \Delta U + nR\Delta T$

$\Delta S = \frac{3}{2} nR \ln \frac{T_f}{T_i} + \cancel{\frac{3}{2} nR \ln\left(\frac{V_f}{V_i}\right)} \rightarrow \emptyset$

c) reversible isothermal expansion, $P_f = 3P_i$ $\quad$ $P_1V_1 = P_2V_2$
$\downarrow$
$T = 310K$ $\quad$ $1 \cdot V_1 = 3 \cdot V_2$
why? $\rightarrow$ $\Delta T = \emptyset$ $\quad$ $3 \quad 1$
$\downarrow$

$\Delta U = \cancel{\frac{3}{2} nR\Delta T}$ $\emptyset$ $\quad$ $\Delta U = \Delta H = \emptyset$ $\quad$ $w = -q = -nR\ln\left(\frac{V_f}{V_i}\right)$ $\quad$ $V_f = 3$, $V_i = 1$

Dropping pressure means volume goes up proportionally

$\Delta S = \cancel{\frac{3}{2} nR \ln \frac{T_f}{T_i}}^{\emptyset} + nR\ln\frac{V_f}{V_i}$