(P4.1)
(a) the number of microstates is $2^{N}$
(b) 3 particles total
$\Rightarrow p_{\{2 H, 1 T\}}=\frac{3!}{2!* 1!}=3$ number microstates of specific arrangement (macrostate)
probability $=(\#$ microstates of specific arrangement $) /($ total \# of microstates $)$
prob $=\frac{3}{2^{3}}=\frac{3}{8}$
(c ) \# microstates.
$p_{\{2 H, 2 T\}}=\frac{4!}{2!* 2!}=6$
$p_{\{3 H, 2 T\}}=\frac{5!}{3!* 2!}=10$
$p_{\{4 H, 2 T\}}=\frac{6!}{4!* 2!}=15$
$p_{\{3 H, 3 T\}}=\frac{6!}{3!* 3!}=20$
(d)

| macrostate |  | \# of microstates* |
| :---: | :---: | :--- |
| H | T |  |
| 0 | 8 | 1 |
| 1 | 7 | 8 |
| 2 | 6 | 28 |
| 3 | 5 | 56 |
| 4 | 4 | 70 |
| 5 | 3 | 56 |
| 6 | 2 | 28 |
| 7 | 1 | 8 |
| 8 | 0 | 1 |

* number of microstates $=\frac{8!}{m!(8-m)!}$
total number of microstates is $2^{8}=256$, which is the same as the sum from the table. portion of microstates (probability) for requested configurations:
$\{5: 3\}=56 / 256=0.219=22 \%$
$\{4: 4\}=70 / 256=0.273=27 \%$
$\{3: 5)=22 \%$ like $\{5: 3\}$
probability of any one of the three most evenly distributed states $=22 \%+27 \%+22 \%=$ 71\%
(e) for 8 particle system, Stirling's approx will not apply
$\Delta \underline{\mathrm{S}} / \mathrm{k}=\ln (\mathrm{p}\{4: 4\} / \mathrm{p}\{5: 3\})=\ln (70 / 56)=0.223$
(P4.2) Initial (each $x$ represents 5 molecule)

| xxxx |  |
| :--- | :--- |
|  |  |

Final

| $x$ | $x$ |
| :--- | :--- |
| $x$ | $x$ |

Create a space with a three empty boxes for the initial state. The number of molecules is too small to use Stirling's approximation.
$\mathrm{p} 1=20!/(20!0!0!0!)=1$
$\mathrm{p} 2=20!/(5!5!5!5!)=20 * 19 * 18 * 17 * 16 * 15 * 14 * 13 * 12 * 11 * 10 * 9 * 8 * 7 * 6 /(5 * 4 * 3 * 2)^{\wedge} 3=$ 11732745024
$\Delta \mathrm{S} / \mathrm{k}=\ln (\mathrm{p} 2 / \mathrm{p} 1)=\ln (11732745024)=23.18$
(P4.3) 15 molecules in 3 boxes, molecules are identical

$$
\begin{aligned}
& p_{j}=\frac{N!}{\prod_{i=1} m_{i j}!} \cdots \cdots \cdots \\
& p_{1}=\frac{15!}{9!4!2!}=75075 \\
& p_{2}=\frac{15!}{(5!)^{3}}=756756 \\
& \frac{\Delta S}{k}=\ln \left[\frac{p_{2}}{p_{1}}\right]=2.31
\end{aligned}
$$

(P4.4) two dice.
$\frac{\Delta \underline{S}}{k}=? ?$ for going from double sixes to a four and three.
$\Rightarrow$ for double sixes, we have probability of $1 / 6$ for each dice.
$\Rightarrow p_{1}=\frac{2!}{(1 / 6) *(1 / 6)}$
for one four and one three $\Rightarrow$ probability applied for $1 / 6$ for each one in each dice,
$\Rightarrow p_{2}=\frac{2!}{(1 / 6) \cdot(1 / 6)}{ }^{* 2}$
$\frac{\Delta \underline{S}}{k}=\ln \left(\frac{p_{2}}{p_{1}}\right)=\ln 2=0.693$
(P4.5) $\Delta \mathrm{S}=?$ ?
Assume Nitrogen is an Ideal gas $\Rightarrow \quad P V=R T$ Eqn. 1.12
$\Rightarrow P_{1}=\frac{8.314\left(\mathrm{~cm}^{3} * \mathrm{MPa} / \mathrm{mole}-K\right) * 300 \mathrm{~K}}{23(\mathrm{~L} / \mathrm{mole}) *\left(1000 \mathrm{~cm}^{3} / 1 \mathrm{~L}\right)}=0.108 \mathrm{MPa}$
Similarly $\Rightarrow P_{2}=0.00723 \mathrm{MPa}$
$\Delta S=C p \ln \frac{T_{2}}{T_{1}}-R \ln \frac{P_{2}}{P_{1}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. Eqn. 4.29
$C p=\frac{7 R}{2} \ldots . .(\mathrm{ig})$
$\Delta S=\frac{7 R}{2} * \ln \frac{400}{300}-8.314 * \ln \frac{0.00723}{0.108}=30.88 \mathrm{~J} / \mathrm{mole}-K=1.07 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$
(P4.6) (a) m-balance: $d n^{\text {in }}=-d n^{\text {out }}$
S-balance:
$\frac{d(n S)^{\text {in }}}{d t}=-S^{\text {out }} \frac{d n^{\text {out }}}{d t} \Rightarrow n^{\text {in }} d S^{\text {in }}+S^{\text {in }} d n^{\text {in }}=-S^{\text {out }} d n^{\text {out }}$
But physically, we know that the leaking fluid is at the same state as the fluid in the tank; therefore, the S-balance becomes:
$(n d S+S d n)^{\text {inside }}=-(S d n)^{\text {out }}$, and $d n^{\text {inside }}=-d n^{\text {out }}$ so $\Delta S=0$
from the steam table .

| State | P(Mpa) | $\mathrm{T}^{\circ} \mathrm{C}$ | H(kJ/kg) | S(kJ/kg*K) |
| :---: | :---: | :---: | :---: | :---: |
| 1(in) | 1 | 400 | 3264.5 | 7.4669 |
| 2 (out) | 0.1 | 120.8 | 2717.86 | 7.4669 |


| At 1 bar $=$ | $\mathbf{0 . 1 ~ M P a ~}$ |
| :--- | :--- |
| $\boldsymbol{T}$ | $\mathbf{S}$ |
| 100 | 7.361 |
| $\mathbf{1 2 0 . 8}$ | 7.4669 |
| 150 | 7.6148 |

By interpolation, implies $T=120 . \mathbf{8}^{\circ} \mathrm{C}$
(P4.7) (a) Steady-state flow, $\Delta \mathrm{H}=\mathrm{Ws}$


Start 1 mole basis:
$x_{1}=0.333, x_{2}=0.667$, adiabatic, $C p=x_{1} C p_{1}+x_{2} C p_{2}, C p$ for each is the same anyway.
$M W=x_{1} M W_{1}+x_{2} M W_{2}=0.333(12+16)+0.667 * 2=10.66(\mathrm{~g} / \mathrm{mole})$
$R=1.987 \mathrm{BTU} / \mathrm{lbmol}-\mathrm{R}$.
$\Delta H=W_{S}=\int_{T_{1}}^{T_{2}} C p d T=\frac{7}{2} * R *(1100-100)^{\circ} R$
$\Rightarrow \Delta H=6954.5 B T U / \mathrm{lbmol}$
\& $\dot{m}=1$ ton $/ h=2000 \mathrm{lb} / \mathrm{h}$.
$\& M W=10.66 \mathrm{lb} / \mathrm{lbmol}$
$\Rightarrow \Delta H=\frac{2000 \mathrm{lb}}{\mathrm{h}} * \frac{\mathrm{lbmol}}{10.66 \mathrm{lb}} * \frac{6954.5 \mathrm{BTU}}{\mathrm{lbmol}}$
$\Rightarrow \Delta H=W_{S}=1,305,000=1.3 * 10^{6} \mathrm{BTU} / \mathrm{h}$
(b) $\eta=$ ?? of the compressor.

To accompany Introductory Chemical Engineering Thermodynamics © J.R. Elliott, C.T. Lira, 2001-2014, all rights reserved. (11/26/2014)

To find the efficiency of the compressor, $\Rightarrow S_{1}=S_{2}$
But the enthalpy and the internal energy will change which gives a change in the

$$
\begin{aligned}
& \text { Work. } \Rightarrow \eta=\frac{W_{S}}{W_{S}}=? ? \\
& \Delta S=0=C p \ln \frac{T_{2}^{\prime}}{T_{1}}-R \ln \frac{P_{2}}{P_{1}} \\
& \Rightarrow C p \ln \frac{T_{2}^{\prime}}{T_{1}}=R \ln \frac{P_{2}}{P_{1}} \\
& \Rightarrow\left(\frac{T_{2}^{\prime}}{T_{1}}\right)^{C_{p}}=\left(\frac{P_{2}}{P_{1}}\right)^{R} \\
& \Rightarrow T_{2}^{\prime}=\left(\frac{P_{2}}{P_{1}}\right)^{\frac{R}{C_{p}}} * T_{1} \\
& \Rightarrow T_{2}^{\prime}=\left(\frac{100}{5}\right)^{\frac{2}{7}} * 559 R \\
& T_{2}^{\prime}=1315 R \\
& \& \Delta H^{\prime}=C p\left(T_{2}^{\prime}-T_{1}\right)=6.95(1315-559) \Rightarrow \eta=\frac{\Delta H^{\prime}}{\Delta H}=\frac{5258}{6955}=0.76 \\
& \Rightarrow \Delta H^{\prime}=5258 B T U / \operatorname{lbmol}
\end{aligned}
$$

(P4.8) Adiabatic, steady-state open system $\Rightarrow \mathrm{Q}=0, \&(\mathrm{Cp} / \mathrm{R}=7 / 2) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. ig
$W=\int_{300}^{625} C p d T=\frac{7 R}{2} *(625-300)=9457.175 \mathrm{~kJ} / \mathrm{kmole} * \frac{1 \mathrm{kmole}}{28 \mathrm{~kg}}=337.76 \mathrm{~kJ} / \mathrm{kg}$ $\eta=?$ ?
$\Delta S=0 \Rightarrow \frac{T_{2}^{\prime}}{T_{1}}=\left(\frac{P_{2}}{P_{1}}\right)^{\frac{R}{C_{p}}}$
$\Rightarrow T_{2}^{\prime}=533.5 \mathrm{~K}$
$\Rightarrow \Delta H^{\prime}=C p\left(T_{2}^{\prime}-T_{1}\right)=\left(\frac{7 * 8.314}{2}\right) *(533.5-300)$
$\Rightarrow \Delta H^{\prime}=6794.77 \mathrm{~kJ} / \mathrm{mol}$
$\Rightarrow \eta=\frac{\Delta H^{\prime}}{\Delta H}=\frac{6794.77 \mathrm{~kJ} / \mathrm{kmol}}{337.76 \mathrm{~kJ} / \mathrm{kg} * 28 \mathrm{~kg} / \mathrm{kmol}}=0.718$
$\Rightarrow \eta=71.8 \%$
(P4.9) work required per kg of steam through this compressor?
By looking at the steam table in the back of the book

| $\mathrm{P}(\mathrm{MPa})$ | $\mathrm{T}\left({ }^{\circ} \mathrm{C}\right)$ | $\mathrm{H}(\mathrm{kJ} / \mathrm{kg})$ | $\mathrm{S}(\mathrm{kJ} / \mathrm{kg}-\mathrm{K})$ |
| :--- | :--- | :--- | :--- |

To accompany Introductory Chemical Engineering Thermodynamics

| 0.8 | 200 | 2839.7 | 6.8176 |
| ---: | ---: | ---: | ---: |
| 4 | 500 | 3446 | 7.0922 |

$W=\Delta H=3446-2839.7=606.3 \mathrm{~kJ} / \mathrm{kg}$
now find $\mathrm{W}^{\prime}=$ ??
$\Delta \mathrm{S}=0$ (reversible), $\Rightarrow$ look in the steam table $(@ \mathrm{P}=4.0 \mathrm{MPa})$ to find a similar value for $S=6.8176 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$, if this value is not available so find it by interpolation.

$$
\begin{aligned}
& \text { H(kJ/kg) } \quad \mathrm{S}(\mathrm{~kJ} / \mathrm{kg}-\mathrm{K}) \\
& 3214.5 \quad 6.7714 \\
& \mathrm{H}^{\prime}=\text { ?? } \mathrm{S}^{\prime}=6.8176 \\
& 3331.2 \quad 6.9386 \\
& \Rightarrow \frac{3331.5-H^{\prime}}{3331.2-3214.5}=\frac{6.9386-6.8176}{6.9386-6.7714}, \Rightarrow H^{\prime}=3246.7 \\
& \Rightarrow \Delta H^{\prime}=W^{\prime}=3246.7-2839.7=407 \mathrm{~kJ} / \mathrm{kg} \\
& \Rightarrow \eta=\frac{407}{606.3}=0.67, \Rightarrow \eta=67 \%
\end{aligned}
$$

(P4.10)@ $\mathrm{P}=2.0 \mathrm{MPa} \& \mathrm{~T}=600^{\circ} \mathrm{C}, \Rightarrow \mathrm{H}=3690.7 \mathrm{~kJ} / \mathrm{kg}, \mathrm{S}=7.7043 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$ (Steam table)

|  | ${ }^{\mathrm{O}} \mathrm{C}$ | $\mathrm{H}_{\mathrm{L}}(\mathrm{kJ} / \mathrm{kg})$ | $\Delta \mathrm{H}^{\text {vap }}(\mathrm{kJ} / \mathrm{kg})$ |
| :--- | ---: | ---: | ---: |
| steam table | 20 | 83.91 | 2453.52 |
| Interpolation | 24 | 100.646 | 2444.098 |
| steam table | 24 | 104.83 | 2441.68 |

$$
\begin{aligned}
& H=H_{L}+q\left(\Delta H^{V a p}\right)=1006.46+0.98 *(2441.68)=2493 \mathrm{k} .49 \mathrm{~J} / \mathrm{kg} \\
& \Rightarrow W_{S}=\Delta H=3690.7-2493.49=1197.21 \mathrm{~kJ} / \mathrm{kg} \\
& \eta=? ?, \quad \eta=\frac{\Delta H}{\Delta H^{\prime}}=\frac{W}{W^{\prime}},
\end{aligned}
$$

$\Rightarrow \Delta S=0$ ( reversible), $\Rightarrow$ look for S in the sat'd temp. steam table and find H by interpolation, $\Rightarrow W^{\prime}=1408.0 \mathrm{~kJ} / \mathrm{kg}$

$$
\Rightarrow \eta=\frac{1197.2}{1408.0}=0.8503, \Rightarrow \eta=85 \%
$$

(P4.11)

$$
\begin{aligned}
& P_{1}=0.1 \mathrm{MPa}, \text { Sat' } d_{\text {vap }} \\
& P_{2}=10 \mathrm{MPa} \\
& T_{2}=1100^{\circ} \mathrm{C}
\end{aligned}
$$

| State | $P(\mathrm{MPa})$ | $\mathrm{T}\left({ }^{\circ} \mathrm{C}\right)$ | $\mathrm{H}(\mathrm{kJ} / \mathrm{kg})$ | $\mathrm{S}(\mathrm{kJ} / \mathrm{kg}-\mathrm{K})$ |
| :--- | :--- | :--- | :--- | :--- |

Chapter 4 Practice Problems

| 1 | 0.1 | 99.61 | 2674.95 | 7.3589 |
| ---: | ---: | ---: | ---: | ---: |
| $2^{\prime}$ | 10 |  | 4062.53 | 7.3589 |
| 2 | 10 | 1100 | 4870.3 | 8.0288 |

interpolation for above table:

| $\mathrm{H}_{2}=4062.53$ | (interpolation) |
| :--- | :--- |
| $\mathbf{H}(\mathbf{k J / k g})$ | $\mathbf{S}(\mathbf{k J} / \mathbf{k g}-\mathrm{K})$ |
| 3992 | 7.2916 |
| 4062.53 | 7.3589 |
| 4114.5 | 7.4085 |

$\Rightarrow \Delta H=W_{S}=4870.3-2674.95=2195.35 \mathrm{~kJ} / \mathrm{kg}$
mass flow rate $=1 \mathrm{~kg} / \mathrm{s}$
$\Rightarrow \dot{W}_{s}=2195.35 \mathrm{~kJ} / \mathrm{s}=2195350 \mathrm{watt}$
\& 1watt $=0.001341022 h p$
$\Rightarrow \dot{W}_{s}=2944.01 \mathrm{hp}$
$\& \Delta H^{\prime}=4062.53-2674.95=1387.58 \mathrm{~kJ} / \mathrm{kg}$
$\Rightarrow \eta=\frac{\Delta H^{\prime}}{\Delta H}=\frac{1387.58}{2195.35}=0.63$
$\Rightarrow \eta=63.2 \%$
(P4.12)
Ebal: $\Delta H=W$.
Sbal: $\Delta S^{\text {rev }}=0 \Rightarrow\left(\frac{T_{2}^{\text {rev }}}{T_{1}}\right)=\left(\frac{P_{2}}{P_{1}}\right)^{\left(\frac{R}{C_{p}}\right)} \Rightarrow T_{2}^{\text {rev }}=(20+273)^{*} 18^{\wedge}(8.314 / 44)=506 \mathrm{~K}$.
$W^{\text {rev }}=C_{p}\left(T_{2}{ }^{\text {rev }}-T_{1}\right)=44^{*}(506-293)=9372 \mathrm{~J} / \mathrm{mol} \Rightarrow W_{\text {act }}=9372 / 0.85=13.4 \mathrm{~kJ} / \mathrm{mol}$
$W^{\text {act }}=C_{p}\left(T_{2}{ }^{\text {act }}-T_{1}\right)=13400=>T_{2}{ }^{\text {act }}=(13400 / 44)+293=597 \mathrm{~K}$
(P4.15) Through the valve $\Rightarrow H^{\text {in }}=H^{\text {out }}$

$$
P^{\text {in }}=3 \mathrm{MPa} \quad P^{\text {out }}=0.1 \mathrm{MPa} \quad T_{\text {out }}=110^{\circ} \mathrm{C}=383.15 \mathrm{~K}
$$

(By interpolation) Find $H^{\text {out }}$ from steam table.

$$
\begin{aligned}
& \frac{150-110}{150-100}=\frac{2776.6-H^{\text {out }}}{2776.6-2675.8} \\
& \Rightarrow H^{\text {out }}=2695.96 \mathbf{~ k J} / \mathbf{k g}
\end{aligned}
$$

At 3 MPa table use same value for $\boldsymbol{H}^{\boldsymbol{i n}}$ to find $\boldsymbol{S}^{\boldsymbol{i n}}$
$\Rightarrow$ By interpolation $\frac{2856.5-2695.96}{2856.5-2803.2}=\frac{6.2893-S^{i n}}{6.2893-6.1856}$
$\Rightarrow S^{\text {in }}=5.976 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$
To accompany Introductory Chemical Engineering Thermodynamics © J.R. Elliott, C.T. Lira, 2001-2014, all rights reserved. (11/26/2014)

The process should be irreversible. To find $S^{\text {out }}$, interpolate using temperature at 0.1 MPa :
$\frac{150-110}{150-100}=\frac{7.6148-S^{\text {out }}}{7.6148-7.3610}$
$S^{\text {out }}=7.4118 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$, since $\mathrm{S}^{\text {out }}>\mathrm{S}^{\text {in }}$ entropy has been generated. The entropy balance is:

$$
0=S^{\text {in }} \dot{m}^{\text {in }}-S^{\text {out }} \dot{m}^{\text {out }}+\dot{S}_{\text {gen }}
$$

(P4.18) An insulated cylinder is fitted with a freely floating piston, ...
Steam $0.5 \mathrm{~kg}, P^{i}=9$ bars, $q=0.9$, goes to satd vapor at 30 bars, $\underline{W}_{\text {air }}=-360 \mathrm{~kJ}$.
The volume change of the air is equal and opposite the volume change of the steam. The volume change of the steam is (using sat properties at 0.9 MPa )
$\underline{V}_{\text {steam }}^{i}=0.5 \mathrm{~kg}\left(V^{\text {satL }}+q\left(V^{\text {satV }}-V^{\text {satL }}\right)\right) \mathrm{m}^{3} / \mathrm{kg}=0.5(0.001121+0.9(0.2149-.001121))=$ $0.09676 \mathrm{~m}^{3}$
$\underline{V}_{\text {steam }}^{f}=0.5^{*} V^{\text {satV }}=0.5 \mathrm{~kg}^{*} .0667 \mathrm{~m}^{3} / \mathrm{kg}=0.03335 \mathrm{~m}^{3}$;
$\Delta V_{\text {steam }}=0.03335-0.09876=-0.06541 \mathrm{~m}^{3}$.
$\underline{V}_{\text {fir }}=\underline{V}_{\text {iir }}^{i}+\Delta \underline{V}_{\text {air }}=0.05+0.06541=0.1154 \mathrm{~m}^{3}$
Because we are not told the mass and area of the piston, let us consider it massless, so that the initial pressure of the air is 9 bar and the final pressure is 30 bar . The air will be treated like an ideal gas.
$d(n U)=H^{\text {in }} d n+d$ Wair; integrate term-by-term
$n^{f} U^{f}-n^{i} U^{i}=H^{i n}\left(n^{f}-n^{i}\right)-360$
for the air, let $H_{R}=0$ for 50 bar and 300 K , the inlet condition.
$n^{i}=P \underline{V} / R T=0.9 \mathrm{MPa}\left(0.05 \mathrm{~m}^{3}\right)\left(10^{6} \mathrm{~cm}^{3} / \mathrm{m}^{3}\right) / 8.31447\left(\mathrm{~cm}^{3}-\mathrm{MPa}\right) / 300=18.041$ moles
$n^{f}=P \underline{V} / R T=3 \mathrm{MPa}\left(0.1154 \mathrm{~m}^{3}\right)\left(10^{6} \mathrm{~cm}^{3} / \mathrm{m}^{3}\right) / 8.31447\left(\mathrm{~cm}^{3}-\mathrm{MPa}\right) / T_{\text {air }}^{f}=41638 / T_{\text {air }}^{f}$ moles
Let $H_{R}=0$ at 50 bar and $300 \mathrm{~K} \Rightarrow U_{R}=H_{R}(P V)=0-R T_{R}=-2494.3 \mathrm{~J} / \mathrm{mol}$
Because $U$ is independent of $P$, then $U^{i}=U_{R}=-2494.3 \mathrm{~J} / \mathrm{mol}$.
For air, use $\mathrm{Cv}=2.5 \mathrm{R}=20.786 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
The energy balance becomes
41638/T ${ }_{\text {air }}^{f}$ [20.786( $\left.\left.T_{\text {air }}^{f}-300\right)-2494.3\right] \mathrm{J}=-360000 \mathrm{~J}$
Trial\&Error $\Rightarrow T_{f}=297 \mathrm{~K}$; the temperature change is very small for this case.

