# Thermodynamics 

Petroleum Engineering
Second year

Properties of Pure Substances

## Property Table

* For example if the pressure and specific volume are specified, three questions are asked: For the given pressure,



## Property Table

* If the answer to the first question is yes, the state is in the compressed liquid region, and the compressed liquid table is

$$
v<v_{f}
$$ used to find the properties. (or using saturation temperature table)

* If the answer to the second question is yes, the state is in the saturation region, and either the saturation temperature table or the saturation pressure table is used.
* If the answer to the third question is yes, the state is in the superheated region and

$$
v_{g}<v
$$ the superheated table is used.



## Example 2.1

## Determine the saturated pressure, specific volume, internal energy and enthalpy for saturated water vapor at $45^{\circ} \mathrm{C}$ and $50^{\circ} \mathrm{C}$.

Saturated water-Temperature table

| Temp. <br> $T^{\circ} \mathrm{C}$ | Sat. press., $P_{\text {sat }} \mathrm{kPa}$ | Specific volume, $\mathrm{m}^{3} / \mathrm{kg}$ |  | Internal energy, $\mathrm{kJ} / \mathrm{kg}$ |  |  | Enthalpy, $\mathrm{kJ} / \mathrm{kg}$ |  |  | Entropy, $\mathrm{kJ} / \mathrm{kg} \cdot \mathrm{K}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Sat. liquid, $v_{f}$ | Sat. vapor, $v_{g}$ | Sat. liquid, $u_{f}$ | $\begin{aligned} & \text { Evap., } \\ & u_{f g} \end{aligned}$ | Sat. <br> vapor, <br> $U_{g}$ | Sat. liquid, $h_{f}$ | Evap., $h_{f g}$ | Sat. vapor, $h_{g}$ | Sat. liquid, $s_{f}$ | $\begin{aligned} & \text { Evap., } \\ & s_{f g} \end{aligned}$ | Sat. vapor, $S_{g}$ |
| 0.01 | 0.6117 | 0.001000 | 206.00 | 0.000 | 2374.9 | 2374.9 | 0.001 | 2500.9 | 2500.9 | 0.0000 | 9.1556 | 9.1556 |
| 5 | 0.8725 | 0.001000 | 147.03 | 21.019 | 2360.8 | 2381.8 | 21.020 | 2489.1 | 2510.1 | 0.0763 | 8.9487 | 9.0249 |
| 10 | 1.2281 | 0.001000 | 106.32 | 42.020 | 2346.6 | 2388.7 | 42.022 | 2477.2 | 2519.2 | 0.1511 | 8.7488 | 8.8999 |
| 15 | 1.7057 | 0.001001 | 77.885 | 62.980 | 2332.5 | 2395.5 | 62.982 | 2465.4 | 2528.3 | 0.2245 | 8.5559 | 8.7803 |
| 20 | 2.3392 | 0.001002 | 57.762 | 83.913 | 2318.4 | 2402.3 | 83.915 | 2453.5 | 2537.4 | 0.2965 | 8.3696 | 8.6661 |
| 25 | 3.1698 | 0.001003 | 43.340 | 104.83 | 2304.3 | 2409.1 | 104.83 | 2441.7 | 2546.5 | 0.3672 | 8.1895 | 8.5567 |
| 30 | 4.2469 | 0.001004 | 32.879 | 125.73 | 2290.2 | 2415.9 | 125.74 | 2429.8 | 2555.6 | 0.4368 | 8.0152 | 8.4520 |
| 35 | 5.6291 | 0.001006 | 25.205 | 146.63 | 2276.0 | 2422.7 | 146.64 | 2417.9 | 2564.6 | 0.5051 | 7.8466 | 8.3517 |
| 40 | 7.3851 | 0.001008 | 19.515 | 167.53 | 2261.9 | 2429.4 | 167.53 | 2406.0 | 2573.5 | 0.5724 | 7.6832 | 8.2556 |
| 45 | 9.5953 | 0.001010 | 15.251 | 188.43 | 2247.7 | 2436.1 | 188.44 | 2394.0 | 2582.4 | 0.6386 | 7.5247 | 8.1633 |
| 50 | 12.352 | 0.001012 | 12.026 | 209.33 | 2233.4 | 2442.7 | 209.34 | 2382.0 | 2591.3 | 0.7038 | 7.3710 | 8.0748 |
| 55 | 15.163 | 0.001015 | 9.5639 | 230.24 | 2219.1 | 2449.3 | 230.26 | 2369.8 | 2600.1 | 0.7680 | 7.2218 | 7.9898 |

## Example 2.2

## Determine the saturated pressure, specific volume, internal energy and enthalpy for saturated water vapor at $47^{\circ} \mathrm{C}$.

Saturated water-Temperature table

|  |  | Specific volume, $\mathrm{m}^{3} / \mathrm{kg}$ |  | Internal energy, $\mathrm{kJ} / \mathrm{kg}$ |  |  | Enthalpy, $\mathrm{kJ} / \mathrm{kg}$ |  |  | Entropy, <br> $\mathrm{kJ} / \mathrm{kg} \cdot \mathrm{K}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Temp. $T^{\circ} \mathrm{C}$ | Sat. press., $P_{\text {sat }} \mathrm{kPa}$ | Sat. liquid, $v_{f}$ | Sat. vapor, $v_{g}$ | Sat. liquid, $u_{f}$ | Evap., $u_{f g}$ | Sat. <br> vapor, $U_{g}$ | Sat. liquid, $h_{f}$ | $\begin{aligned} & \text { Evap., } \\ & h_{f g} \end{aligned}$ | Sat. <br> vapor, $h_{g}$ | Sat. liquid, $s_{f}$ | $\begin{aligned} & \text { Evap., } \\ & s_{f g} \end{aligned}$ | Sat. vapor, $S_{g}$ |
| 0.01 | 0.6117 | 0.001000 | 206.00 | 0.000 | 2374.9 | 2374.9 | 0.001 | 2500.9 | 2500.9 | 0.0000 | 9.1556 | 9.1556 |
| 5 | 0.8725 | 0.001000 | 147.03 | 21.019 | 2360.8 | 2381.8 | 21.020 | 2489.1 | 2510.1 | 0.0763 | 8.9487 | 9.0249 |
| 10 | 1.2281 | 0.001000 | 106.32 | 42.020 | 2346.6 | 2388.7 | 42.022 | 2477.2 | 2519.2 | 0.1511 | 8.7488 | 8.8999 |
| 15 | 1.7057 | 0.001001 | 77.885 | 62.980 | 2332.5 | 2395.5 | 62.982 | 2465.4 | 2528.3 | 0.2245 | 8.5559 | 8.7803 |
| 20 | 2.3392 | 0.001002 | 57.762 | 83.913 | 2318.4 | 2402.3 | 83.915 | 2453.5 | 2537.4 | 0.2965 | 8.3696 | 8.6661 |
| 25 | 3.1698 | 0.001003 | 43.340 | 104.83 | 2304.3 | 2409.1 | 104.83 | 2441.7 | 2546.5 | 0.3672 | 8.1895 | 8.5567 |
| 30 | 4.2469 | 0.001004 | 32.879 | 125.73 | 2290.2 | 2415.9 | 125.74 | 2429.8 | 2555.6 | 0.4368 | 8.0152 | 8.4520 |
| 35 | 5.6291 | 0.001006 | 25.205 | 146.63 | 2276.0 | 2422.7 | 146.64 | 2417.9 | 2564.6 | 0.5051 | 7.8466 | 8.3517 |
| 40 | 7.3851 | 0.001008 | 19.515 | 167.53 | 2261.9 | 24294 | 167.53 | 2406.0 | 2573.5 | 0.5724 | 7.6832 | 8.2556 |
| 45 | 9.5953 | 0.001010 | 15.251 | 188.43 | 2247.7 | 2436.1 | 188.44 | 2394.0 | 2582.4 | 0.6386 | 7.5247 | 8.1633 |
| 50 | 12.352 | 0.001012 | 12.026 | 209.33 | 2233.4 | 2442.7 | 209.34 | 2382.0 | 2591.3 | 0.7038 | 7.3710 | 8.0748 |
| 55 | 15.763 | 0.001015 | 9.5639 | 230.24 | 2219.1 | 2449.3 | 230.26 | 2369.8 | 2600.1 | 0.7680 | 7.2218 | 7.9898 |

## Solution:

$\square$ Extract data from steam table

| $\boldsymbol{T}$ | $P_{\text {sat }}$ | v | u | $\boldsymbol{h}$ |
| :---: | :---: | :---: | :---: | :---: |
| 45 | 9.5953 | 15.251 | 2436.1 | 2582.4 |
| 47 | $P_{\text {sat }}$ | $v$ | $u$ | $h$ |
| 50 | 12.352 | 12.026 | 2442.7 | 2591.3 |

$\square$ Interpolation for $P_{\text {sat }}$

$$
\begin{aligned}
\frac{P_{\text {sat }}-9.5953}{12.352-9.5953} & =\frac{47-45}{50-45} \\
P_{\text {sat } Q 47^{\circ}} & =\underline{\underline{10.698 \mathrm{kPa}}}
\end{aligned}
$$

- Do the same principal to others!!!!


Interpolation Scheme for $P_{\text {sat }}$

## Exercises

1. Fill in the blank using R-134a

| $\mathrm{T}\left({ }^{\circ} \mathrm{C}\right)$ | $\mathrm{P}(\mathrm{kPa})$ | $\mathrm{h}(\mathrm{kJ} / \mathrm{kg})$ | x | Phase description |
| :---: | :---: | :---: | :---: | :---: |
|  | 600 | 180 |  |  |
| -10 |  |  | 0.6 |  |
| -14 | 500 |  |  |  |
|  | 1200 | 300.61 |  |  |
| 44 |  |  | 1.0 |  |

2. Determine the saturated temperature, saturated pressure and enthalpy for water at specific volume of saturated vapor at $10.02 \mathrm{~m}^{3} / \mathrm{kg}$.

## Example 2.3

Determine the enthalpy of 1.5 kg of water contained in a volume of $1.2 \mathrm{~m}^{3}$ at 200 kPa .

## Solution:

$\square$ Specific volume for water

$$
v=\frac{\text { Volume }}{\text { mass }}=\frac{1.2 \mathrm{~m}^{3}}{1.5 \mathrm{~kg}}=0.8 \frac{\mathrm{~m}^{3}}{\mathrm{~kg}}
$$

$\square$ From table A-5:

$$
\begin{aligned}
& v_{f}=0.001061 \mathrm{~m}^{3} / \mathrm{kg} \\
& v_{g}=0.8858 \mathrm{~m}^{3} / \mathrm{kg}
\end{aligned}
$$

Is $v<v_{f}$ ? No
Is $v_{f}<v<v_{g}$ ? Yes
Is $v_{g}<v$ ? No
$\square$ Find the quality

$$
\begin{aligned}
v & =v_{f}+x\left(v_{g}-v_{f}\right) \\
x & =\frac{v-v_{f}}{v_{g}-v_{f}} \\
& =\frac{0.8-0.001061}{0.8858-0.001061} \\
& =0.903 \text { (What does this mean?) }
\end{aligned}
$$

$\square$ The enthalpy

$$
\begin{aligned}
h & =h_{f}+x h_{f g} \\
& =504.7+(0.903)(2201.6) \\
& =2492.7 \frac{\mathrm{~kJ}}{\mathrm{~kg}}
\end{aligned}
$$

## Example 2.4

Determine the internal energy of refrigerant-134a at a temperature of $0^{\circ} \mathrm{C}$ and a quality of $60 \%$.

## Solution:

* From table A-5:

$$
\begin{aligned}
& u_{f}=51.63 \frac{\mathrm{~kJ}}{\mathrm{~kg}} \\
& u_{g}=230.16 \frac{\mathrm{~kJ}}{\mathrm{~kg}}
\end{aligned}
$$

* The internal energy of R 134a at given condition:

$$
\begin{aligned}
u & =u_{f}+x\left(u_{g}-u_{f}\right) \\
& =51.63+(0.6)(230.16-51.63) \\
& =158.75 \frac{\mathrm{~kJ}}{\mathrm{~kg}}
\end{aligned}
$$

## Example 2.5

Consider the closed, rigid container of water as shown. The pressure is 700 kPa , the mass of the saturated liquid is 1.78 kg , and the mass of the saturated vapor is 0.22 kg . Heat is added to the water until the pressure increases to 8 MPa. Find the final temperature, enthalpy, and internal energy of the
 water

## Solution:

* Theoretically:

$$
v_{2}=v_{1}
$$

The quality before pressure increased (state 1).

$$
\begin{aligned}
x_{1} & =\frac{m_{g 1}}{m_{f 1}+m_{g 1}} \\
& =\frac{0.22 \mathrm{~kg}}{(1.78+0.22) \mathrm{kg}}=0.11
\end{aligned}
$$

* Specific volume at state 1

$$
\begin{aligned}
v_{1} & =v_{f 1}+x_{1}\left(v_{g 1}-v_{f 1}\right) \\
& =0.001108+(0.11)(0.2728-0.001108) \\
& =0.031 \frac{m^{3}}{k g}
\end{aligned}
$$

## State 2:

* Information :

$$
P_{2}=8 M P a \quad v_{2}=0.031 \frac{m^{3}}{k g}
$$

* From table A-5:

$$
\begin{aligned}
& v_{f, 2}=0.001384 \frac{\mathrm{~m}^{3}}{\mathrm{~kg}} \\
& v_{g, 2}=0.02352 \frac{\mathrm{~m}^{3}}{\mathrm{~kg}}
\end{aligned}
$$

Since that it is in superheated region, use table A-6:

$$
\begin{aligned}
& T_{2}=361.8^{\circ} \mathrm{C} \\
& h_{2}=3024 \frac{\mathrm{~kJ}}{\mathrm{~kg}} \\
& u_{2}=2776 \frac{\mathrm{~kJ}}{\mathrm{~kg}}
\end{aligned}
$$

## Exercises

1. Four kg of water is placed in an enclosed volume of $1 \mathrm{~m}^{3}$. Heat is added until the temperature is $150^{\circ} \mathrm{C}$. Find ( a ) the pressure, ( b )the mass of vapor, and (c) the volume of the vapor.
2. A piston-cylinder device contains $0.1 \mathrm{~m}^{3}$ of liquid water and $0.9 \mathrm{~m}^{3}$ of water vapor in equilibrium at 800 kPa . Heat is transferred at constant pressure until the temperature reaches $350^{\circ} \mathrm{C}$.
(a) what is the initial temperature of the water,
(b) determine the total mass of the water,
(c) calculate the final volume, and
(d) show the process on a $\mathrm{P}-\mathrm{v}$ diagram with respect to saturation lines.

## Exercises

3. For a specific volume of $0.2 \mathrm{~m}^{3} / \mathrm{kg}$, find the quality of steam if the absolute pressure is (a) 40 kPa and (b) 630 kPa . What is the temperature of each case?
4. Water is contained in a rigid vessel of $5 \mathrm{~m}^{3}$ at a quality of 0.8 and a pressure of 2 MPa . If the a pressure is reduced to 400 kPa by cooling the vessel, find the final mass of vapor $m_{g}$ and mass of liquid $m_{f}$

## Important Definition

- Critical point - the temperature and pressure above which there is no distinction between the liquid and vapor phases.
- Triple point - the temperature and pressure at which all three phases can exist in equilibrium.
- Sublimation - change of phase from solid to vapor.
- Vaporization - change of phase from liquid to vapor.
- Condensation - change of phase from vapor to liquid.
- Fusion or melting - change of phase from solid to liquid.



## Ideal Gas Law

Robert Boyle formulates a well-known law that states the pressure of a gas expanding at constant temperature varies inversely to the volume, or

$$
P_{1} V_{1}=P_{2} V_{2}=\text { constant }
$$

As the result of experimentation, Charles concluded that the pressure of a gas varies directly with temperature when the volume is held constant, and the volume varies directly with temperature when the pressure is held constant, or

$$
\frac{V_{1}}{V_{2}}=\frac{T_{1}}{T_{2}} \quad \text { or } \quad \frac{P_{1}}{P_{2}}=\frac{T_{1}}{T_{2}}
$$

* By combining the results of Charles' and Boyl
experiments, the followi
relationship can be obtained
* The constant in the above equation is called the ideal gas constant and is designated by

$$
P v=R T \quad \text { or } \quad P V=m R T
$$

$R$; thus the ideal gas equation becomes

* In order to make the equation applicable to all ideal gas, a universal gas constant $R_{\mathrm{U}}$ is

$$
R=\frac{R_{U}}{M}
$$ introduced

$\square$ For example the ideal gas constant for air, $R_{\text {air }}$

$$
R_{\text {air }}=\frac{\left(R_{U}\right)_{a i r}}{(M)_{a i r}}=\frac{8.3144}{28.96}=0.2871 \mathrm{~kJ} / \mathrm{kg} . \mathrm{K}
$$

T. The amount of energy needed to raise the temperature of a unit of mass of a substance by one degree is called the specific heat at constant volume $C_{V}$ for a constant-volume process and the specific heat at constant pressure $C_{p}$ for a constant pressure process. They are defined as

$$
C_{v}=\left(\frac{\partial u}{\partial T}\right)_{v} \quad \text { and } \quad C_{P}=\left(\frac{\partial h}{\partial T}\right)_{P}
$$

$\square$ Using the definition of enthalpy ( $h=u+P v$ ) and writing the differential of enthalpy, the relationship between the specific heats for ideal gases is

$$
\begin{aligned}
& h=u+P v \\
& d h=d u+R T \\
& C_{P} d t=C_{V} d t+R d T \\
& C_{P}=C_{V}+R
\end{aligned}
$$

- The specific heat ratio, $k$ is defined as

$$
k=\frac{C_{P}}{C_{v}}
$$

$>$ For ideal gases $u, h, C_{\triangleright}$ and $C_{p}$ are functions of temperature alone. The $\Delta u$ and $\Delta h$ of ideal gases can be expressed as

$$
\begin{aligned}
& \Delta u=u_{2}-u_{1}=C_{v}\left(T_{2}-T_{1}\right) \\
& \Delta h=h_{2}-h_{1}=C_{P}\left(T_{2}-T_{1}\right)
\end{aligned}
$$

## Example 2.6

An ideal gas is contained in a closed assembly with an initial pressure and temperature of 220 kPa and $70^{\circ} \mathrm{C}$ respectively. If the volume of the system is increased 1.5 times and the temperature drops to $15^{\circ} \mathrm{C}$, determine the final pressure of the gas.

## Solution:

## given

state 1
$P_{1}=220 \mathrm{kPa}$
$T_{1}=70+273 \mathrm{~K}=343 \mathrm{~K}$
state 2

$$
\begin{aligned}
& T_{2}=15+273=288 K \\
& V_{2}=1.5 V_{1}
\end{aligned}
$$

From ideal-gas law:

$$
\begin{aligned}
\frac{P_{1} V_{1}}{T_{1}} & =\frac{P_{2} V_{2}}{T_{2}} \\
P_{2} & =\frac{V_{1}}{1.5 V_{1}}\left(\frac{288}{343}\right)\left(220 \times 10^{3}\right) \\
& =123.15 \mathrm{kPa}
\end{aligned}
$$

## Example 2.7

A closed assembly contains 2 kg of air at an initial pressure and temperature of 140 kPa and $210^{\circ} \mathrm{C}$ respectively. If the volume of the system is doubled and temperature drops to $37^{\circ} \mathrm{C}$, determine the final pressure of the air. Air can be modeled as an ideal gas.

## Solution:

## given

state 1
$P_{1}=140 \mathrm{kPa}$
$T_{1}=210+273 K=483 K$
state 2

$$
\begin{aligned}
& T_{2}=37+273=310 \mathrm{~K} \\
& V_{2}=2 V_{1}
\end{aligned}
$$

* From ideal-gas law:

$$
\begin{aligned}
\frac{P_{1} V_{1}}{T_{1}} & =\frac{P_{2} V_{2}}{T_{2}} \\
P_{2} & =\frac{V_{1}}{2 V_{1}}\left(\frac{310}{483}\right)\left(140 \times 10^{3}\right) \\
& =44.93 \mathrm{kPa}
\end{aligned}
$$

## Example 2.8

An automobile tire with a volume of $0.6 \mathrm{~m}^{3}$ is inflated to a gage pressure of 200 kPa . Calculate the mass of air in the tire if the temperature is $20^{\circ} \mathrm{C}$.

## Solution:

given

$$
\begin{aligned}
& \text { state } \\
& P=200+100 \mathrm{kPa} \\
& T=20+273 \mathrm{~K}=293 \mathrm{~K}
\end{aligned}
$$

From ideal-gas law:

$$
\begin{aligned}
m & =\frac{P V}{R T} \\
& =\frac{300 \times 10^{3} \frac{\mathrm{~N}}{\mathrm{~m}^{3}}\left(0.6 \mathrm{~m}^{2}\right)}{287 \frac{\mathrm{Nm}}{\mathrm{~kg} \cdot \mathrm{~K}}(293 \mathrm{~K})} \\
& =2.14 \mathrm{~kg}
\end{aligned}
$$

## Supplementary Problems

1. The pressure in an automobile tire depends on the temperature of the air in the tire. When the air temperature is $25^{\circ} \mathrm{C}$, the pressure gage reads 210 kPa . If the volume of the tire is 0.025 m 3 , determine the pressure rise in the tire when the air temperature in the tire rises to $50^{\circ} \mathrm{C}$. Also, determine the amount of air that must be bled off to restore pressure to its original value at this temperature. Assume the atmospheric pressure is 100 kPa .
[ $26 \mathrm{kPa}, 0.007 \mathrm{~kg}$ ]
2. A $1-\mathrm{m}^{3}$ tank containing air at $25^{\circ} \mathrm{C}$ and 500 kPa is connected through a valve to another tank containing 5 kg of air at $35^{\circ} \mathrm{C}$ and 200 kPa . Now the valve is opened, and the entire system is allowed to reach thermal equilibrium with the surroundings, which are at $20^{\circ} \mathrm{C}$. Determine the volume of the second tank and the final equilibrium pressure of air.
[ $2.21 \mathrm{~m}^{3}, 284.1 \mathrm{kPa}$ ]
3. A $1 \mathrm{~m}^{3}$ rigid tank has propane at $100 \mathrm{kPa}, 300 \mathrm{~K}$ and connected by a valve to another tank of $0.5 \mathrm{~m}^{3}$ with propane at $250 \mathrm{kPa}, 400 \mathrm{~K}$. The valve is opened and the two tanks come to a uniform state at 325 K . What is the final pressure?
[ 139.9 kPa ]
4. A cylindrical gas tank 1 m long, inside diameter of 20 cm , is evacuated and then filled with carbon dioxide gas at $25^{\circ} \mathrm{C}$. To what pressure should it be charged if there should be 1.2 kg of carbon dioxide?
[ 2152 kPa ]
