AME 50531
Intermediate Thermodynamics
Examination 2: Solution
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1. (40) Helium and argon exist in a chamber with total pressure $P=100 \mathrm{kPa}$, temperature $T=300 K, V=10 \mathrm{~m}^{3}$. These noble gases are well described as an ideal mixture of inert calorically perfect ideal gases. The mass fraction of helium is 0.5 .
(a) Find the mole fractions of helium and argon.
(b) The mixture is heated isochorically until $T=1000 \mathrm{~K}$. Find the heat transfer to the mixture.

## Solution

The mole fraction of species $i, y_{i}$ can be related to the mass fraction of species $i, c_{i}$ via the equation

$$
y_{i}=\frac{c_{i} / M_{i}}{\sum_{j=1}^{N} c_{j} / M_{j}}
$$

We have

$$
\begin{gathered}
M_{H e}=4 \mathrm{~kg} / \mathrm{kmole} \\
M_{A r}=40 \mathrm{~kg} / \mathrm{kmole}
\end{gathered}
$$

Now the mass fraction of each species is $c_{H e}=0.5, c_{A r}=0.5$. So the mole fractions are

$$
\begin{gathered}
y_{H e}=\frac{c_{H e} / M_{H e}}{c_{H e} / M_{H e}+c_{A r} / M_{A r}}, \\
y_{H e}=\frac{0.5 / 4}{0.5 / 4+0.5 / 40} \\
y_{H e}=0.909091
\end{gathered}
$$

So

$$
y_{A r}=1-y_{H e}=1-0.909091=0.0909091
$$

The first law holds that

$$
U_{2}-U_{1}=Q_{12}-W_{12}
$$

Since the process is isochoric, $W_{12}=0$, so

$$
\begin{aligned}
Q_{12} & =U_{2}-U_{1} \\
& =n_{H e} \bar{u}_{H e 2}+n_{A r} \bar{u}_{A r 2}-n_{H e} \bar{u}_{H e 1}-n_{A r} \bar{u}_{A r 1} \\
& =n_{H e} \bar{c}_{v H e}\left(T_{f}-T_{i}\right)+n_{A r} \bar{c}_{v A r}\left(T_{2}-T_{1}\right) \\
& =\left(n_{H e} \bar{c}_{v H e}+n_{A r} \bar{c}_{v A r}\right)\left(T_{2}-T_{1}\right)
\end{aligned}
$$

Now

$$
P_{H e 1}=y_{H e} P_{1}=.909091(100 k P a)=90.9091 k P a
$$

$$
P_{A r 1}=y_{A r} P_{1}=0.0909091(100 k P a)=9.09091 k P a .
$$

From the ideal gas law and Dalton's law, we have

$$
\begin{aligned}
& n_{H e}=\frac{P_{H e 1} V}{\bar{R} T_{1}}=(90.9091)(10) /(8.314)(300)=0.364 \text { kmole } \\
& n_{A r}=\frac{P_{A r 1} V}{\bar{R} T_{1}}=(9.09091)(10) /(8.314)(300)=0.0364 \text { kmole }
\end{aligned}
$$

Now for the specific heats, one finds

$$
\begin{aligned}
& \bar{c}_{v H e}=c_{v H e} M_{H e}=\left(3.116 \frac{\mathrm{~kJ}}{\mathrm{kgK}}\right)\left(4 \frac{\mathrm{~kg}}{\mathrm{kmole}}\right)=12.464 \frac{\mathrm{~kJ}}{\mathrm{kmole} \mathrm{~K}} \\
& \bar{c}_{v A r}=c_{v A r} M_{A r}=\left(0.312 \frac{\mathrm{~kJ}}{\mathrm{~kg} \mathrm{~K}}\right)\left(40 \frac{\mathrm{~kg}}{\mathrm{kmole}}\right)=12.48 \frac{\mathrm{~kJ}}{\mathrm{kmole} \mathrm{~K}}
\end{aligned}
$$

Note the remarkable fact that on a molar basis, the specific heats of helium and argon are essentially identical! This is not a coincidence, but a fundamental property of noble gases.

So the heat transfer is

$$
Q_{12}=((0.364)(12.464)+(0.0364)(12.48))(1000-300)=3498 k J
$$

2. (40) When a material which is solid at standard temperature and pressure is subjected to a strong shock, all of the elastic bonds are broken, and it behaves as a dense gas. A common model for such a material is the so-called Tait equation. In canonical form, the specific Helmholtz free energy of such a material is sometimes modelled by

$$
a(v, T)=c_{v} T\left(1-\ln \left(\frac{T}{T_{o}}\right)+(k-1) \ln \left(\frac{v_{o}}{v}\right)\right)+\frac{\varepsilon}{k} \frac{v}{v_{o}} .
$$

Here constant parameters are specific heat $c_{v}$, reference temperature and specific volume $v_{o}$ and $T_{o}$, ratio of specific heats $k$, and configuration energy $\varepsilon$. Find the entropy $s(v, T)$, the thermal state equation $P(v, T)$ and caloric state equation $u(v, T)$.

## Solution

Start with the Gibbs equation

$$
d u=T d s-P d v
$$

Recall the definition of $a$ :

$$
a \equiv u-T s
$$

So

$$
d a=d u-T d s-s d T
$$

Eliminate $d u$ in the Gibbs equation to get

$$
d a+T d s+s d T=T d s-P d v
$$

Simplify to get

$$
d a=-s d T-P d v
$$

So the canonical variables for $a$ are $a(T, v)$. Moreover

$$
\left.\frac{\partial a}{\partial v}\right|_{T}=-P,\left.\quad \frac{\partial a}{\partial T}\right|_{v}=-s
$$

Taking $\left.\frac{\partial a}{\partial v}\right|_{T}$, we find

$$
-\frac{c_{v}(k-1) T}{v}+\frac{\varepsilon}{k v_{o}}=-P
$$

So the thermal state equation is

$$
P(v, T)=c_{v}(k-1) \frac{T}{v}-\frac{\varepsilon}{k v_{o}}
$$

Taking $\left.\frac{\partial a}{\partial T}\right|_{v}$, we find

$$
-c_{v}+c_{v}\left(1-\ln \left(\frac{T}{T_{o}}\right)+(k-1) \ln \left(\frac{v_{o}}{v}\right)\right)=-s
$$

So that

$$
s(v, T)=c_{v}\left(\ln \left(\frac{T}{T_{o}}\right)-(k-1) \ln \left(\frac{v_{o}}{v}\right)\right)
$$

Now from the definition of $a$, we have

$$
u=a+T s
$$

Combining and simplifying, we get

$$
u(v, T)=c_{v} T+\frac{\varepsilon}{k} \frac{v}{v_{o}}
$$

3. (20) Consider $100 m^{3}$ of atmospheric air, which is an air-water vapor mixture at $100 \mathrm{kPa}, 15 \mathrm{C}$, and $40 \%$ relative humidity. Find the mass of water in the mixture.

## Solution

First get the humidity ratio

$$
\omega=0.622 \frac{\phi P_{g}}{P-\phi P_{g}}
$$

At $15 C$, the saturated steam tables give

$$
P_{g}=1.705 k P a
$$

So

$$
\omega=0.622 \frac{0.40(1.705)}{100-0.40(1.705)}=0.00427
$$

Now the pressure of the air is

$$
P_{a}=P-P_{v}=P-\phi P_{g}=100-0.4(1.705)=99.318 k P a
$$

The mass of the air is then

$$
m_{a}=\frac{P_{a} V}{R_{a} T}=\frac{99.318(100)}{0.287(15+273)}=120.158 \mathrm{~kg}
$$

So the mass of the vapor is

$$
m_{v}=\omega m_{a}=0.00427(120.158)=0.513 \mathrm{~kg}
$$

