Slide 7

EXAMPLE

Compute the change in enthalpy and entropy for water being pumped from an initial pressure of 101.3 kPa and 20 °C to 3000 kPa and 60 °C. The volume expansivity of water is 6.48 $(10^{-4})K^{-1}$ at 60 °C and 3000 kPa and the heat capacity of water is 75.3 J/(mol K).

Given: $T_1 = 20°C = 293$ K $T_2 = 60$ °C $= 333$ K

$P_1 = 101.3$ kPa $P_2 = 3000$ kPa

$\beta = 6.48 \times 10^{-4}\ K^{-1}$ recalling that $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$C_P = 75.3\ J\ mol^{-1}\ K^{-1}$

Find ΔH and ΔS?

At the initial and final conditions water is a liquid well below the saturation (boiling) point (e.g., subcooled). Check a P-V phase diagram or the steam tables to confirm if necessary.

We will use: $dH = C_P dT + V(1-\beta T)dP$ and $dS = C_P \frac{dT}{T} - \beta V dP$

To calculate the integrals of these state functions we need to define a path.

Choose: Step 1 Isobaric Heating (i.e., dP = 0)
Step 2 Isothermal Compression (i.e., dT = 0)

This is a logical choice because we have β at T_2.

Lastly, because we are dealing with a liquid we will assume that C_P is constant (i.e, not a function of T)

$$\Delta H = \int_{T_1}^{T_2} C_P dT + \int_{P_1}^{P_2} V(1-\beta T)dP$$ where C_P is independent of temperature and the molar volume of liquid water is independent of pressure for the range of the integral. Note that the first integral is for step 1 (where dP = 0) and the second integral is for step 2 where dT = 0.

$$\begin{aligned}
\Delta H &= C_P(T_2 - T_1) + V(1-\beta T_2)(P_2 - P_1) \\
&= 75.3 \frac{\text{J}}{\text{mol K}}(60 - 20)\text{K} + 18.1 \frac{\text{cm}^3}{\text{mol}}(1 - 6.48\times10^{-4}\ \text{K}^{-1}\ 333\ \text{K})(3000 - 101.3)\text{kPa} \\
&= 3012 \frac{\text{J}}{\text{mol}} + 41145 \frac{\text{cm}^3\text{kPa}}{\text{mol}}\left(\frac{1\,\text{L}}{1000\ \text{cm}^3}\right) \\
&= 3053 \frac{\text{J}}{\text{mol}}
\end{aligned}$$

Recalling that 1 Joule = 1 L kPa

Similarly for entropy:

$$\Delta S = \int_{T_1}^{T_2} C_P \frac{dT}{T} - \int_{P_1}^{P_2} (\beta V)dP$$

$$\begin{aligned}
\Delta S &= C_P \ln\frac{T_2}{T_1} - (\beta V)(P_2 - P_1) \\
&= 75.3 \frac{\text{J}}{\text{mol K}} \ln\left(\frac{333}{293}\right) - \left(6.48\times10^{-4}\ \text{K}^{-1}\ 18.1 \frac{\text{cm}^3}{\text{mol}}\right)(3000 - 101.3)\text{kPa} \\
&= 9.64 \frac{\text{J}}{\text{mol K}} - 30.0 \frac{\text{cm}^3\text{kPa}}{\text{mol K}}\left(\frac{1\,\text{L}}{1000\ \text{cm}^3}\right) \\
&= 9.61 \frac{\text{J}}{\text{mol K}}
\end{aligned}$$

Note that **P** has a relatively small effect on **H** and **S** because liquid water is a relatively incompressible fluid.

Slide 8

EXAMPLE

Estimate the change in temperature of liquid water initially at 25 ºC being compressed from 1 atm to 200 atm.

Given: $T_1 = 25^oC = 298$ K $P_1 = 1$ atm
$T_2 = ??$ $P_2 = 200$ atm

Recall that liquid water is relatively incompressible.

As a first estimate, assume that the process occurs **isentropically** (e.g., **dS = 0**)

$$dS = C_P \frac{dT}{T} - \beta V dP = 0$$

Re-arranging

$$C_P \frac{dT}{T} = \beta V dP$$

Assume that the temperature change is small and hence β is constant and that C_P is also constant.

We can therefore integrate:

$$\int_{T_1}^{T_2} C_P \frac{dT}{T} = \int_{P_1}^{P_2} \beta V dP$$

$$C_P \ln \frac{T_2}{T_1} = \beta V \left(P_2 - P_1\right)$$

Solving for T_2 gives:

$$\ln \frac{T_2}{T_1} = \frac{\beta V}{C_P}\left(P_2 - P_1\right)$$

$$\Rightarrow T_2 = T_1 \exp\left(\frac{\beta V}{C_P}\left(P_2 - P_1\right)\right)$$

From tables of thermodynamic data: $C_P = 75.3$ J mol^{-1} K^{-1}

Assuming a small temperature change we can use the value of β for T_1 and check the assumption later.

$\beta = 2.56 \times 10^{-4}$ K^{-1}

Substituting values gives:

$$T_2 = 298\ [\mathrm{K}]\exp\left(\frac{\left(2.56\times 10^{-4}\ \mathrm{K}^{-1}\right)\left(18.1\ \mathrm{cm}^3\ \mathrm{mol}^{-1}\right)}{75.3\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}}(200-1)[\mathrm{atm}]\right)$$

$$= 298\,\mathrm{K}\ \ \exp\left(0.0122\left[\mathrm{cm}^3\ \mathrm{atm\ J}^{-1}\right]\frac{8.314\,\mathrm{J\,mol}^{-1}\mathrm{K}^{-1}}{82.06\ \mathrm{cm}^3\ \mathrm{atm\ mol}^{-1}\ \mathrm{K}^{-1}}\right)$$

$$= 298\,\mathrm{K}\ \ \exp(0.0012)$$

$$= 298.4\ \mathrm{K}$$

$T_2 = 298.4$ K and hence $\Delta T = 0.4$ K so that the assumption of constant β was correct.