

THERMODYNAMIC PROPERTIES AND CALCULATION

Academic Resource Center



THERMODYNAMIC PROPERTIES

A quantity which is either an attribute of an entire system or is a function of position which is continuous and does not vary rapidly over microscopic distances, except possibly for abrupt changes at boundaries between phases of the system; examples are temperature, pressure, volume, concentration, surface tension, and viscosity. Also known as macroscopic property.



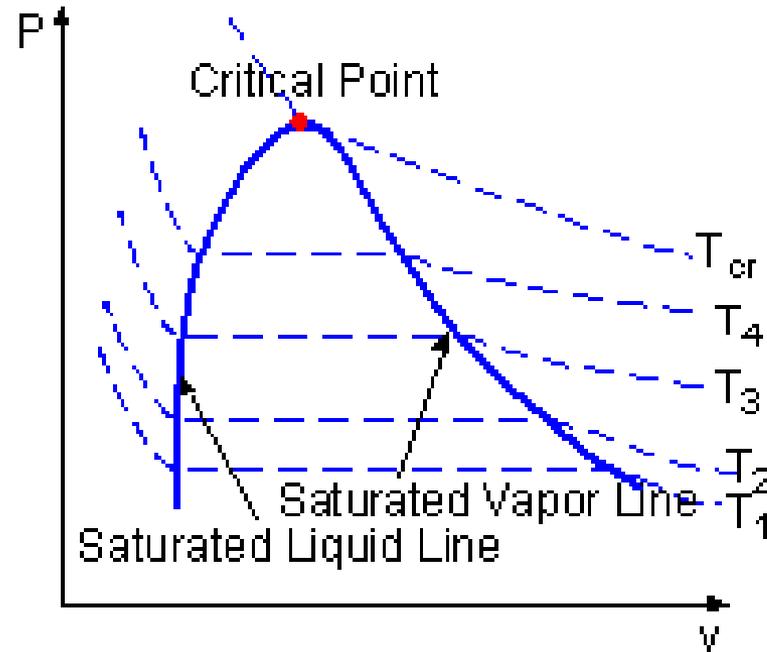
BASIC CONCEPTS-1

- First Law of Thermodynamic:
- Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.
- $\Delta(\text{Energy of the system}) + \Delta(\text{Energy of surroundings}) = 0$
- $\Delta U^t = Q + W \rightarrow \Delta(nU) = Q + W$
- $dU^t = dQ + dW \rightarrow d(nU) = dQ + dW$
- There exists a form of energy, known as internal energy U .



BASIC CONCEPTS-2

- PV diagram



- Virial Equations of State

$$PV = a + bP + cP^2 + \dots$$

$$\rightarrow Z = \frac{PV}{RT} = 1 + BV + CV^2 + \dots$$

- Ideal gas: $Z=1$ or $PV = RT$

- Van Der Waals Equation of State

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$



For Ideal Gas: Equation for Calculation

Heat capacity: $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$ $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$

$$dQ + dW = C_V dT$$

$$dW = -PdV$$

$$dQ = C_V dT + PdV$$

Let $V=RT/P$:

$$dQ = C_V dT + RT \frac{dV}{V}$$

$$dQ = C_P dT - RT \frac{dP}{P}$$

$$dQ = \frac{C_V}{R} V dP + \frac{C_P}{R} P dV$$



BASIC CONCEPTS-3

- Statements of the Second Law:
- Statement 1: No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by a system completely into work done by the system.
- Statement 2: No process is possible which consists solely in the transfer of heat from one temperature level to a higher one



PRIMARY THERMODYNAMIC PROPERTIES— P, V, T, S & U

- Combining the first and second laws in reversible process
- The only requirements are that the system be closed and that the change occur between equilibrium states.
- $H = U + PV$
- $A = U - TS$
- $G = H - TS$

$$d(nU) = Td(nS) - Pd(nV)$$

$$d(nH) = Td(nS) + (nV)dP$$

$$d(nA) = -Pd(nV) - (nS)dT$$

$$d(nG) = (nV)dP - (nS)dT$$

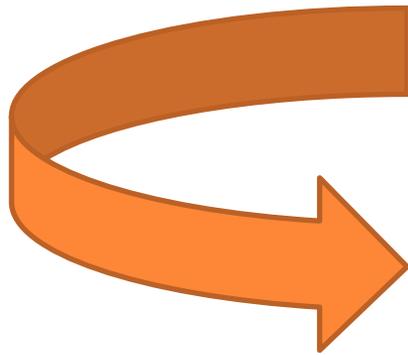


$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -PdV - SdT$$

$$dG = VdP - SdT$$



Maxwell's equation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$



EXAMPLE 1

- Air at 1 bar and 298.15K (25°C) is compressed to 5 bar and 298.15K by two different mechanically reversible processes:
- (a) Cooling at constant pressure followed by heating at constant volume.
- (b) Heating at constant volume followed by cooling at constant pressure.
- Calculate the heat and work requirements and ΔU and ΔH of the air for each path. The following heat capacities for air may be assumed independent of temperature:

$$C_V = 20.78 \text{ and } C_P = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume also for air that PV/T is a constant, regardless of the changes it undergoes. At 298.15K and 1 bar the molar volume of air is $0.02479 \text{ m}^3 \text{ mol}^{-1}$.



KEYS

Definition of enthalpy

$$H \equiv U + PV$$

Heat capacity definition at constant pressure

$$C_p \equiv \left(\frac{\partial H}{\partial T} \right)_p$$

$$dH = C_p dT \text{ (const } P)$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT \text{ (const } P)$$

$$Q = n\Delta H = n \int_{T_1}^{T_2} C_p dT$$

at constant volume

$$C_v \equiv \left(\frac{\partial U}{\partial T} \right)_v$$

$$dU = C_v dT \text{ (const } V)$$

$$\Delta U = \int_{T_1}^{T_2} C_v dT \text{ (const } V)$$

$$Q = n\Delta U = n \int_{T_1}^{T_2} C_v dT$$



SOLUTIONS:

- In such case take the system as 1 mol of air contained in an imaginary piston/cylinder arrangement. Since the processes considered are mechanically reversible, the piston is imagined to move in the cylinder without friction. The final volume is

$$V_2 = V_1 \frac{P_1}{P_2} = 0.02479 \left(\frac{1}{5} \right) = 0.004958 \text{ m}^3$$

- (a) During the first step the air is cooled at the constant pressure of 1 bar until the final volume of 0.004958 m³ is reached. The temperature of the air at the end of this cooling step is:

$$T' = T_1 \frac{V_2}{V_1} = 298.15 \left(\frac{0.004958}{0.02479} \right) = 59.63 \text{ K}$$

$$Q = \Delta H = C_p \Delta T = (29.10)(59.63 - 298.15) = -6,941 \text{ J}$$



SOLUTIONS

- Also,

$$Q = \Delta H - \Delta(PV) = \Delta H - P\Delta V = -6,941 - (1 \times 10^5)(0.004958 - 0.02479) = -4,958\text{J}$$

- During the second step the volume is held constant at while the air is heated to its final state.

$$\Delta U = Q = C_v\Delta T = (20.78)(298.15 - 59.63) = -4,958\text{J}$$

- The complete process represents the sum of its steps. Hence,

$$Q = -6,941 + 4,958 = -1,983\text{J}$$

$$\Delta U = -4,958 + 4,958 = 0\text{J}$$

- Since the first law applies to the entire process, , and therefore,

$$0 = -1,983 + W$$

$$W = 1,983\text{J}$$



SOLUTIONS

- $\Delta H = \Delta U + \Delta(PV)$,
- also applies to the entire process. But

$$T_1 = T_2$$

- and therefore,

$$P_1 V_1 = P_2 V_2$$

- Hence ,

$$\Delta(PV) = 0$$

- and

$$\Delta H = \Delta U = 0$$



SOLUTIONS

- Two different steps are used in this case to reach the same final state of the air. In the first step the air is heated at a constant volume equal to its initial value until the final pressure of 5 bar is reached. The air temperature at the end of this step is:

$$T' = T_1 \frac{P_2}{P_1} = 298.15 \left(\frac{5}{1} \right) = 1,490.75\text{K}$$

- For this step the volume is constant, and

$$\begin{aligned} Q = \Delta U &= C_v \Delta T = (20.78)(1,490.75 - 298.15) \\ &= 24,788\text{J} \end{aligned}$$

- During the second step the air is cooled at the constant pressure of 5 bar to its final state:

$$\begin{aligned} Q = \Delta H &= C_p \Delta T = (29.10)(298.15 - 1,490.75) \\ &= -34,703\text{J} \end{aligned}$$



SOLUTIONS

- Also,

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V = -34,703 - (5 \times 10^5)(0.004958 - 0.02479) = -24,788\text{J}$$

- For the two steps combined,

$$Q = 24,788 - 34,703 = -9,915\text{J}$$

$$\Delta U = 24,788 - 24,788 = 0\text{J}$$

$$W = \Delta U - Q = 0 - (-9,915) = 9,915\text{J}$$

- and as before $\Delta H = \Delta U = 0$
- During the second step the volume is held constant at V_2 while the air is heated to its final state.
- The property changes and calculated for the given change in state are the same for both paths. On the other hand the answers to parts (a) and (b) show that Q and W depend on the path.



EXAMPLE 2

- Air is compressed from an initial condition of 1 bar and 25°C to a final state of 5 bar and 25°C by three different mechanically reversible processes in a closed system:
- (a) Heating at constant volume followed by cooling at constant pressure.
- (b) Isothermal compression.
- (c) Adiabatic compression followed by cooling at constant volume.
- Assume air to be an ideal gas with the constant heat capacities, $C_V = (5/2)R$ and $C_P = (7/2)R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air for each process.



KEYS

Isothermal Process:

$$\Delta H = \Delta U = 0$$

$$Q = -W = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1} \text{ (const T)}$$

Adiabatic Process: constant heat capacities

$$TV^{\gamma-1} = \text{constant}$$

$$TP^{(1-\gamma)/\gamma} = \text{constant}$$

$$PV^{\gamma} = \text{constant}$$

$$W = \Delta U = C_V \Delta T$$



SOLUTIONS

- Choose the system as 1 mol of air, contained in an imaginary frictionless piston/cylinder arrangement. For $R=8.314 \text{ J mol}^{-1}\text{K}^{-1}$,

$$C_V=20.785 \quad C_P=29.099 \text{ J mol}^{-1} \text{ K}^{-1}$$

- The initial and final conditions of the air are identical with those of Ex.1, where the molar volumes are given as:

$$V_1=0.02479 \quad V_2=0.004958 \text{ m}^3$$

- Moreover, since the initial and final temperatures are the same, then for all parts of the problem:

$$\Delta H = \Delta U = 0$$



SOLUTIONS

- (a) The heat transferred, from Ex.1(b) is $Q = -9.915\text{J}$. Thus by the first law applied to the entire process:

$$W = \Delta U - Q = 0 - (-9,915) = 9,915\text{J}$$

- (b) Equation for the isothermal compression of an ideal gas applies here:

$$\begin{aligned} Q = -W &= RT \ln \frac{P_1}{P_2} = (8.314)(298.15) \ln \frac{1}{5} \\ &= -3,990\text{J} \end{aligned}$$

- (c) The initial adiabatic compression of the air takes it to its final volume of 0.004958m^3 . The temperature and pressure at this point are:



SOLUTIONS

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = (298.15) \left(\frac{0.02479}{0.004958} \right)^{0.4} = 567.57\text{K}$$

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^{\gamma} = (1) \left(\frac{0.02479}{0.004958} \right)^{1.4} = 9.52\text{bar}$$

For this step $Q=0$, and

$$W = C_V \Delta T = (20.785)(567.57 - 298.15) = 5,600\text{J}$$

For the second step at constant V , $W=0$. For the overall process,

$$W = 5,600 + 0 = 5,600\text{J}$$



SOLUTIONS

- Moreover, $\Delta U = 0$, and by the first law,

$$Q = \Delta U - W = 0 - 5,600 = -5,600\text{J}$$

- Although the property changes and are zero for each process, Q and W are path-dependent. Since the work for each of these mechanically reversible processes is given by , the work for each process is proportional to the total area below the paths on the PV diagram representing the process. The relative sizes of these areas correspond to the numerical values of W .



EXAMPLE 3

- Determine the enthalpy and entropy changes of liquid water for a change of state from 1 bar and 25 °C to 1,000 bar and 50°C. The following data for water are available:

$t/^\circ\text{C}$	P/bar	$C_p/\text{J mol}^{-1} \text{K}^{-1}$	$V/\text{cm}^3 \text{mol}^{-1}$	β/K^{-1}
25	1	75.305	18.071	256×10^{-6}
25	1,000	18.012	366×10^{-6}
50	1	75.314	18.234	458×10^{-6}
50	1,000	18.174	568×10^{-6}



KEYS

$$\left(\frac{\partial S}{\partial P}\right)_T = -\beta V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = (1 - \beta T)V$$

$$dH = C_p dT + \left[V - T \left(\frac{\partial V}{\partial T}\right)_P \right] dP$$

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dH = C_p dT + (1 - \beta T) V dP$$

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



SOLUTIONS

- For application to the change of state described, equations require integration. Since enthalpy and entropy are state functions, the path of integration is arbitrary. Since the data indicate that C_p is a weak function of T and that both V and β are weak functions of P , integration with arithmetic means is satisfactory. The integrated forms of Eqs that result are:

$$\Delta H = C_p(T_2 - T_1) - (1 - \beta T_2) V(P_2 - P_1)$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} - \beta V(P_2 - P_1)$$



SOLUTIONS

- For $P=1$ bar,

$$C_p = \frac{75.305 + 75.314}{2} = 75.310 \text{ J mol}^{-1} \text{ K}^{-1}$$

- and for $t=50^\circ\text{C}$

$$V = \frac{18.234 + 18.174}{2} = 18.204 \text{ cm}^3 \text{ mol}^{-1}$$

$$\beta = \frac{458 + 568}{2} \times 10^{-6} = 513 \times 10^{-6} \text{ K}^{-1}$$



SOLUTIONS

- Substitution of these numerical values into the equation for ΔH gives:

$$\begin{aligned}\Delta H &= 75.310(323.15 - 298.15) + \frac{[1 - (513 \times 10^{-6})(323.15)](18.204)(1,000 - 1)}{10\text{cm}^3\text{bar J}^{-1}} \\ &= 1,883 + 1,517 = 3,400\text{Jmol}^{-1}\end{aligned}$$

- Similarly for ΔS ,

$$\begin{aligned}\Delta S &= 75.310\ln\frac{323.15}{298.15} - \frac{(513 \times 10^{-6})(18.204)(1,000 - 1)}{10\text{cm}^3\text{bar J}^{-1}} \\ &= 6.06 - 0.93 = 5.13\text{Jmol}^{-1}\text{K}^{-1}\end{aligned}$$

- Note that the effect of a pressure change of almost 1,000 bar on the enthalpy and entropy of liquid water is less than that of a temperature change of only 25°C



THERMODYNAMIC PROPERTIES AND THEIR CHARACTERISTICS

Property	Symbol	Units	Extensive?	Intensive?	Conjugate	Potential?	State qty.?	Process qty.?
Activity	a	-		✓			✓	
Altitude		m	✓				✓	
Chemical potential	μ_i	kJ/mol		✓	Particle number		✓	
Compressibility (adiabatic)	β_S, κ	Pa ⁻¹		✓			✓	
Compressibility (isothermal)	β_T, κ	Pa ⁻¹		✓			✓	
Cryoscopic constant ^[1]	K_f	K·kg/mol						
Density	ρ	kg/m ³		✓			✓	
Ebullioscopic constant	K_b							
Enthalpy	H	J	✓			✓	✓	
↳ Specific enthalpy	h	J/kg		✓			✓	
Entropy	S	J/K	✓		Temperature	✓ (entropic)	✓	
↳ Specific entropy	s	J/(kg K)		✓			✓	
Fugacity	f	N/m ²		✓			✓	
Gas constant	R, \bar{R}	J/K		✓				
↳ Specific gas constant (for a particular substance)	R_S	J/(kg K)		✓				
Gibbs free energy	G	J	✓			✓	✓	
↳ Specific Gibbs free entropy	g	J/(kg K)		✓			✓	
Gibbs free entropy	Ξ	J/K	✓			✓ (entropic)	✓	



Heat	Q	J	✓				✓
Heat capacity (constant pressure)	C_p	J/K	✓				✓
↳ Specific heat capacity (constant pressure)	c_p	J/(kg·K)		✓			✓
Heat capacity (constant volume)	C_v	J/K	✓				✓
↳ Specific heat capacity (constant volume)	c_v	J/(kg·K)		✓			✓
Helmholtz free energy	A, F	J	✓			✓	✓
Helmholtz free entropy	Φ	J/K	✓			✓ (entropic)	✓
Internal energy	U	J	✓			✓	✓
↳ Specific internal energy	u	J/kg		✓			✓
Internal pressure	π_T	Pa		✓			✓
Mass	m	kg	✓				
Particle number	N_i	-	✓		Chemical potential		
Pressure	p	Pa		✓	Volume		✓
Temperature	T	K		✓	Entropy		✓
Thermal conductivity	k	W/(m·K)		✓			✓
Thermal diffusivity	α	m ² /s		✓			✓
Thermal expansion (linear)	α_L	K ⁻¹		✓			✓
Thermal expansion (area)	α_A	K ⁻¹		✓			✓
Thermal expansion (volumetric)	α_V	K ⁻¹		✓			✓
Vapor quality ^[2]	χ	-		✓			✓
Volume	V	m ³	✓		Pressure		✓
↳ Specific volume	v	m ³ /kg		✓			✓
Work	W	J	✓				✓

