Topic 4C - Enthalpy

Thermodynamic Functions

Internal Energy (U)

Sum of all potential energy (intra-molecular bonds & intermolecular interactions) and kinetic energy (translational, rotational, vibrational) contributions to system.

First "Law" of Thermodynamics (conservation of energy):

$\Delta U = q + w$

U = Internal Energy (a state function)

q, w = heat, work (non-state functions)

The algebraic signs of U, q, and w always reflect the system's point of view. Thus, an overall increase in the system's internal energy results in $\Delta U > 0$. An inflow of energy into the system as heat corresponds to $q > 0$. Work performed by the system on the surroundings (*e.g.*, expansion) results in $w < 0$ (*i.e.*, an outflow of energy from the system).

Pressure-Volume Work

For expansion against a constant external pressure:

$$w = -P_{ext}\Delta V$$

Enthalpy

If pressure is constant, and all work is of P-V type, the first law becomes

$$\Delta U = q - P\Delta V$$

Since U, P, and V are all state functions, then at constant P, q is also a state function:

$$q = \Delta U + P\Delta V = \Delta H$$

where the defined state function H is termed the enthalpy.

Heat Capacities

If an ideal monatomic gas is heated in a rigid container (*i.e.*, V is constant), all of the energy transferred into the system as heat is utilized to increase the kinetic energy of the gas atoms (*i.e.*, to increase U and, hence, T), since no P-V work is performed. Since for an ideal gas,

$$(K.E.)_{ave} = 3/2\ RT$$

then the amount of energy that is required to cause a temperature change of ΔT is $3/2\ R\Delta T$.

The molar heat capacity of a substance is the amount of energy that is required to increase the temperature of one mole of the substance by 1 K. Thus, for an ideal monatomic gas, the heat capacity at constant volume, C_v, is given by:

$$C_v = 3/2\ R$$

If an ideal monatomic gas is heated at constant pressure, then part of the added heat energy is utilized to increase the kinetic energy of the gas atoms (*i.e.*, increase T), and part is used to perform P-V work, due to expansion of the gas.

Thus, more energy is required to cause a given increase in temperature at constant pressure of the gas than at constant volume.

Since for one mole of an ideal gas PV = RT, then the P-V work that is performed by the gas on the surroundings during a constant pressure expansion is:

$$-w = P\Delta V = R\Delta T$$

For a temperature increase of 1 K, $R\Delta T = R$. Thus, the total energy required to increase the temperature of one mole of an ideal monatomic gas at constant pressure, *i.e.*, the heat capacity at constant pressure, C_p, is:

$$C_p = 3/2R + R = 5/2\ R$$

or

$$C_p = C_v + R$$

For polyatomic gases, the actual values of C_v and C_p are larger than 3/2 R and 5/2 R, respectively, because part of the added energy is utilized to increase the rotational and vibrational energies of the molecules, in addition to increasing the translational energy (which causes the temperature increase).

Thus, at constant volume (*i.e.*, w=0; no P-V work performed),

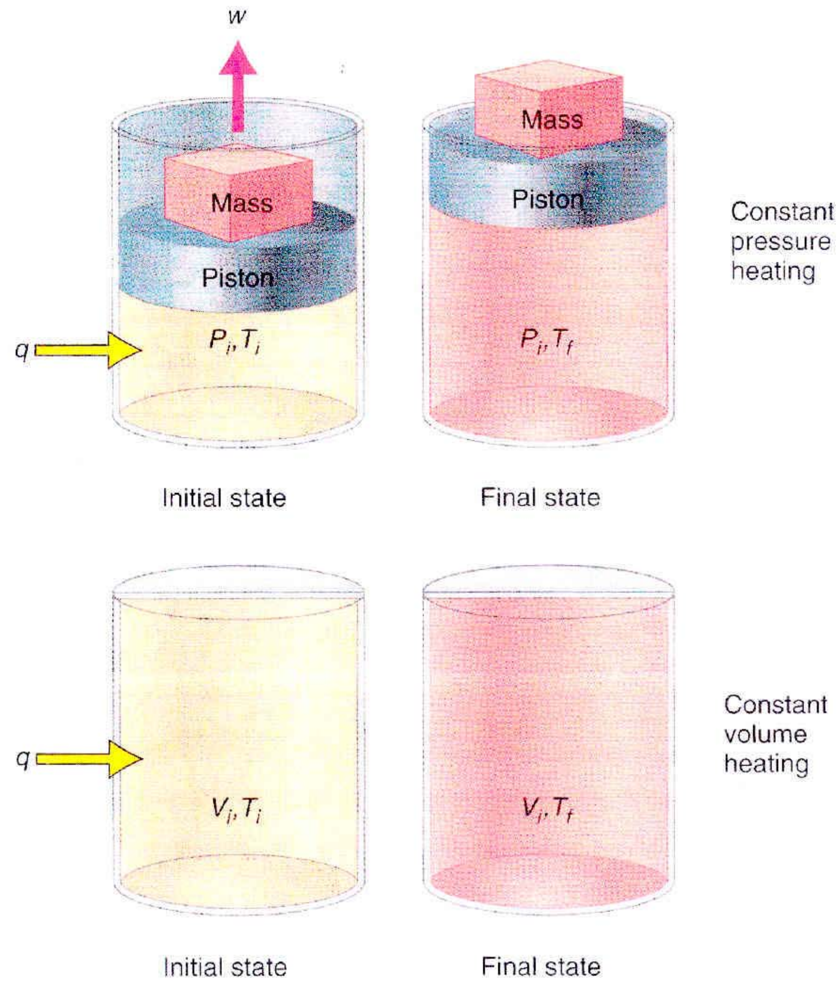
$$\Delta U = q = nC_v\Delta T$$

At constant pressure, (*i.e.*, $|w| \neq 0$; P-V work performed),

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V = \Delta U + nR\Delta T \\ &= nC_v\Delta T + nR\Delta T \\ &= n(C_v + R)\Delta T \\ &= nC_p\Delta T\end{aligned}$$

FIGURE 2.6

Not all the heat flow into the system can be used to increase ΔU in a constant pressure process, because the system does work on the surroundings as it expands. However, no work is done for constant volume heating.



Molar Heat Capacities of Various Gases at 298 K

Gas	C_v (J/mol-K)	C_p (J/mol-K)	$C_p - C_v$
He, Ne, Ar, Kr	12.47 (3/2 R)	20.80 (5/2 R)	8.33 (R)
H_2	20.54	28.86	8.32
N_2	20.71	29.03	8.32
O_2	21.10	29.36	8.26
F_2		31.30	
CO		29.14	
NO		29.84	
N_2O	30.38	38.45	8.32
NO_2		37.20	
CO_2	28.95	37.27	8.32
O_3		39.29	
NH_3		35.06	
CH_4		35.31	
CCl_4		83.30	
C_2H_6	44.60	52.92	8.32
C_6H_6		81.67	

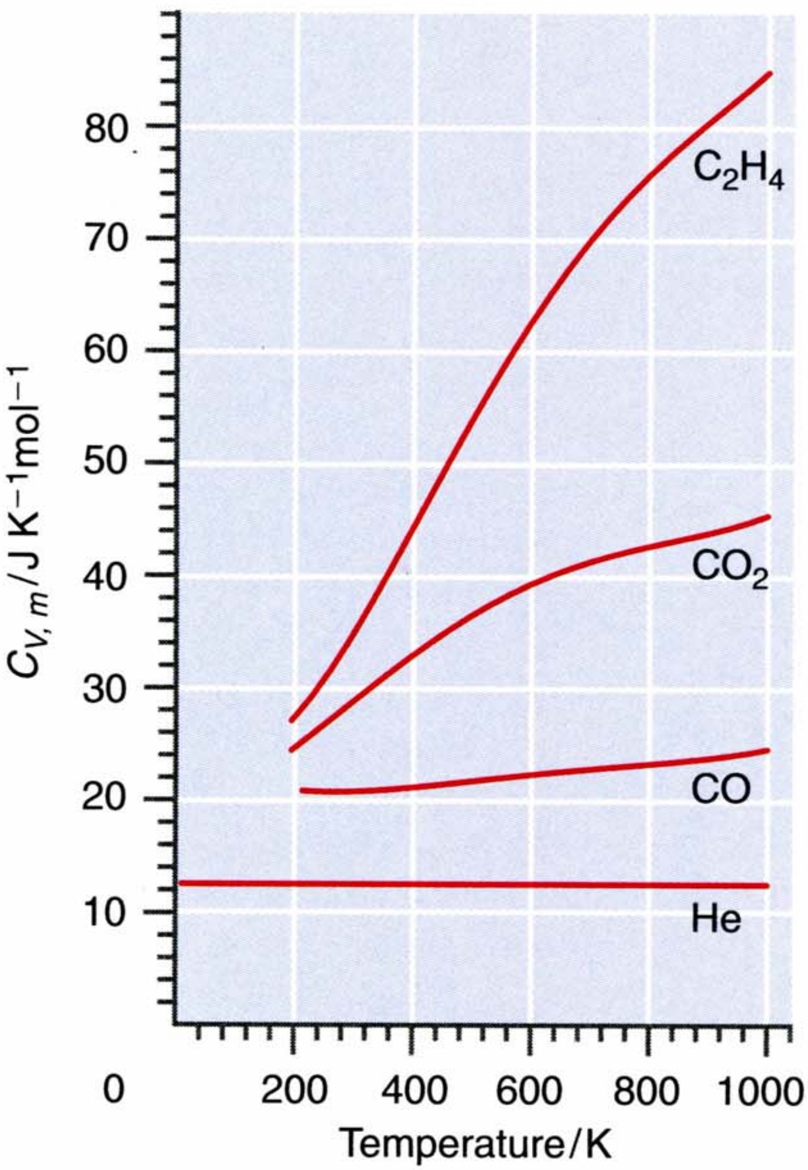


FIGURE 3.2

Molar heat capacities $C_{V,m}$ are shown for a number of gases. Atoms have only translational degrees of freedom and, therefore, have comparatively low values for $C_{V,m}$ that are independent of temperature. Molecules with vibrational degrees of freedom have higher values of $C_{V,m}$, at temperatures sufficiently high to activate the vibrations.

Enthalpy Changes

Physical Processes (changes of state)

Fusion ΔH°_{fus} $(= -\Delta H^\circ_{freezing})$

Vaporization ΔH°_{vap} $(= -\Delta H^\circ_{condensation})$

Sublimation ΔH°_{subl} $(= \Delta H^\circ_{fus} + \Delta H^\circ_{vap})$

Temperature Change $\Delta H^\circ = nC_p\Delta T$

Chemical Reactions

$$\Delta H^\circ_{reaction} = \sum n_{prod}\Delta H^\circ_f\text{ (products)} - \sum n_{react}\Delta H^\circ_f\text{ (reactants)}$$

TABLE 8.3 Standard Enthalpies of Physical Change*

Substance	Formula	Freezing point (K)	ΔH_{fus}° ($kJ \cdot mol^{-1}$)	Boiling point (K)	ΔH_{vap}° ($kJ \cdot mol^{-1}$)
acetone	CH_3COCH_3	177.8	5.72	329.4	29.1
ammonia	NH_3	195.4	5.65	239.7	23.4
argon	Ar	83.8	1.2	87.3	6.5
benzene	C_6H_6	278.6	10.59	353.2	30.8
ethanol	C_2H_5OH	158.7	4.60	351.5	43.5
helium	He	3.5	0.021	4.22	0.084
mercury	Hg	234.3	2.292	629.7	59.3
methane	CH_4	90.7	0.94	111.7	8.2
methanol	CH_3OH	175.2	3.16	337.8	35.3
water	H_2O	273.2	6.01	373.2	40.7 (44.0 at 25 °C)

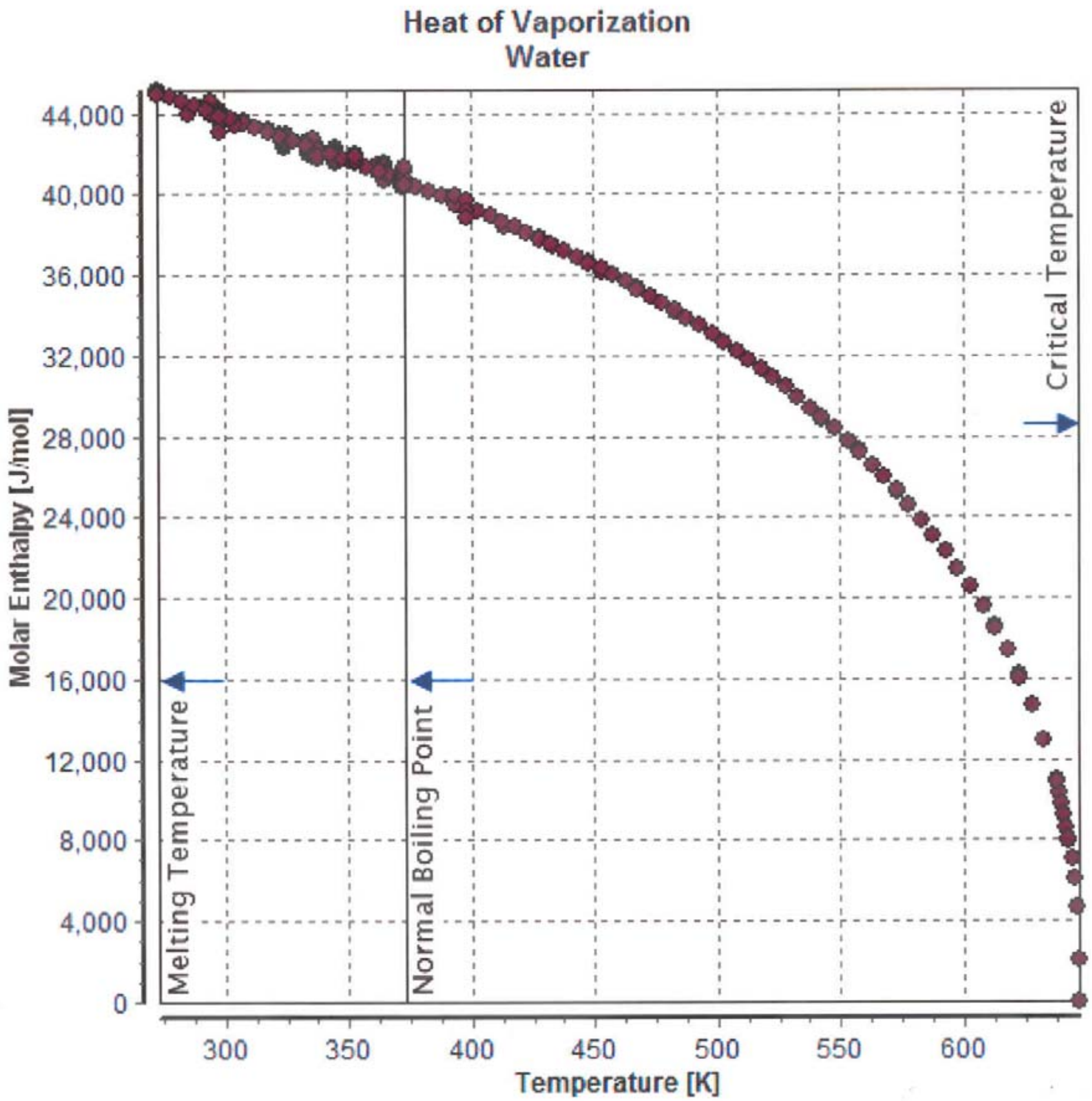
*Values correspond to the temperature of the phase change. The superscript ° signifies that the change takes place at 1 bar and that the substance is pure (that is, the values are for standard states; see Section 8.15).

TABLE 7.2

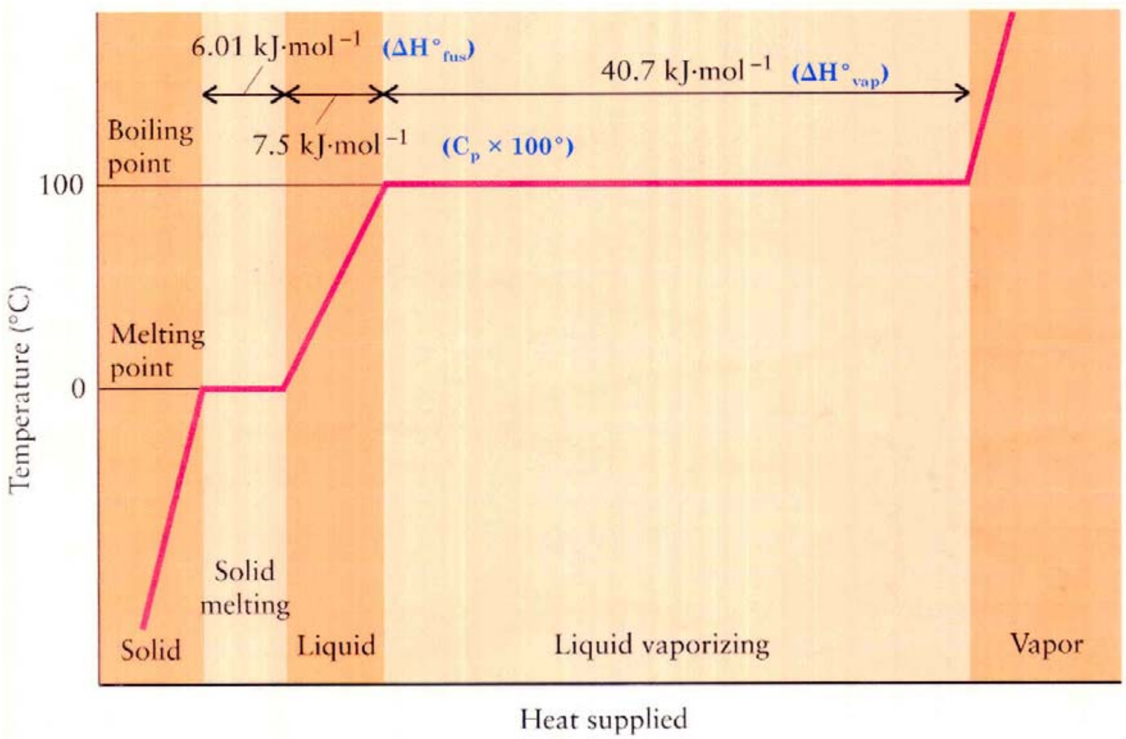
Enthalpy Changes of Fusion and Vaporization†

Substance	ΔH_{fus} (kJ mol^{-1})	ΔH_{vap} (kJ mol^{-1})
NH_3	5.65	23.35
HCl	1.992	16.15
CO	0.836	6.04
CCl_4	2.5	30.0
H_2O	6.007	40.66
NaCl	28.8	170

† The enthalpy changes are measured at the normal melting point and the normal boiling point, respectively.



Heating Curve for Water



Molar Heat Capacities (C_p):

Ice	37.94 J/Mol-K
Water	75.37 "
Steam	35.93 "