Thermodynamics

the study of the transformations of energy from one form into another

First Law: Heat and Work are both forms of Energy. in any process,
Energy can be changed from one form to another (including heat and work),
but it is never created or distroyed: Conservation of Energy

Second Law: Entropy is a measure of disorder; Entropy of an isolated system Increases in any spontaneous process. OR ***This law also predicts that the entropy of an isolated system always increases with time.***

Third Law: The entropy of a perfect crystal approaches zero as temperature approaches absolute zero.

TABLE 7.1 Varieties of work

Type of work	w	Comment	Units*
expansion	$-P_{\text{ex}}\Delta V$	P_{ex} is the external pressure ΔV is the change in volume	Pa m^3
extension	$f\Delta l$	f is the tension Δl is the change in length	N m
raising a weight	$mg\Delta h$	m is the mass g is the acceleration of free fall Δh is the change in height	kg $\text{m}\cdot\text{s}^{-2}$ m
electrical	$\phi\Delta q$	ϕ is the electrical potential Δq is the change in charge	V C
surface expansion	$\gamma\Delta A$	γ is the surface tension ΔA is the change in area	$\text{N}\cdot\text{m}^{-1}$ m^2

*For work in joules (J). Note that 1 N·m = 1 J and 1 V·C = 1 J.

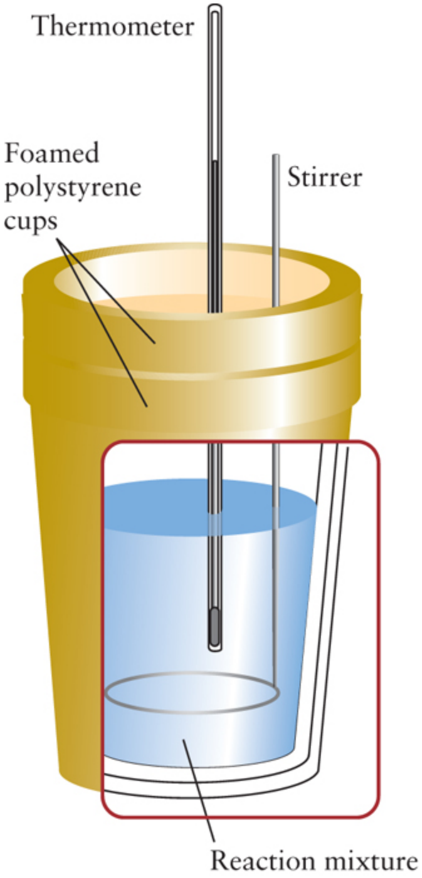


FIGURE 7.11 The energy released or absorbed as heat by a reaction at constant pressure can be measured in this simple calorimeter. The outer polystyrene cup acts as an extra layer of insulation to ensure that no heat enters or leaves the inner cup. The quantity of energy released or absorbed as heat is proportional to the change in temperature of the calorimeter.

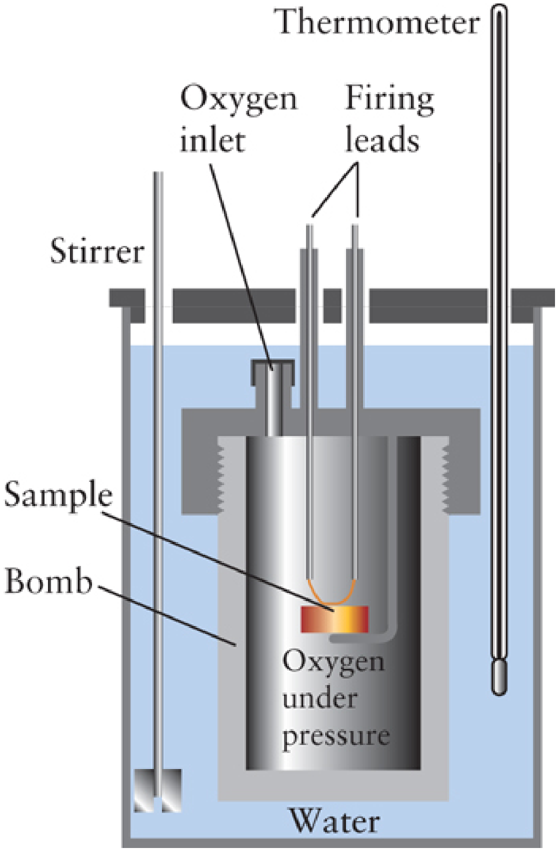


FIGURE 7.12 A bomb calorimeter is used to measure heat transfers at constant volume. The sample in the central rigid container called the bomb is ignited electrically with a fuse wire. Once combustion has begun, energy released as heat spreads through the walls of the bomb into the water. The heat released is proportional to the temperature change of the entire assembly.

TABLE 7.2 Specific and Molar Heat Capacities of Common Materials*

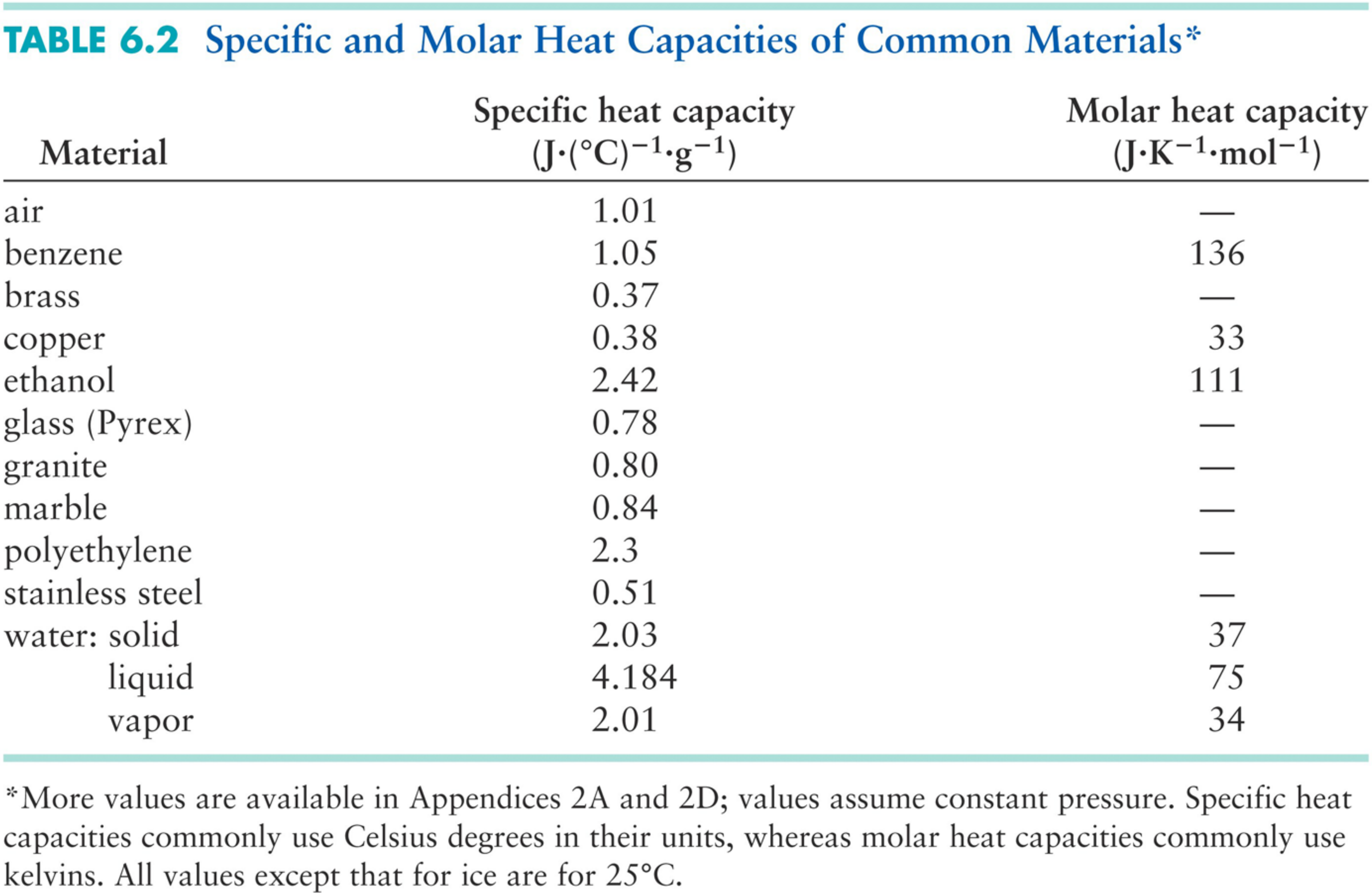


TABLE 6.2 Specific and Molar Heat Capacities of Common Materials*

Material	Specific heat capacity (J·(°C)$^{-1}$·g^{-1})	Molar heat capacity (J·K^{-1}·mol^{-1})
air	1.01	—
benzene	1.05	136
brass	0.37	—
copper	0.38	33
ethanol	2.42	111
glass (Pyrex)	0.78	—
granite	0.80	—
marble	0.84	—
polyethylene	2.3	—
stainless steel	0.51	—
water: solid	2.03	37
liquid	4.184	75
vapor	2.01	34

*More values are available in Appendices 2A and 2D; values assume constant pressure. Specific heat capacities commonly use Celsius degrees in their units, whereas molar heat capacities commonly use kelvins. All values except that for ice are for 25°C.

A Molecular Interlude: Internal Energy, U, from translation, rotation, vibration

- $U_{translation} = 3/2 \times nRT$

- $U_{rotation} = nRT$ (for linear molecules)

  or

- $U_{rotation} = 3/2 \times nRT$ (for nonlinear molecules)

- At room temperature, the vibrational contribution is small (it is of course zero for monatomic gas at any temperature). At some high temperature, it is $(3N-5)nR$ for linear and $(3N-6)nR$ for nolinear molecules (N = number of atoms in the molecule.

Enthalpy

$H = U + PV$

Enthalpy is a state function and at constant pressure:

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

At constant pressure, the change in enthalpy is equal to the heat released or absorbed by the system.

Exothermic: $\Delta H < 0$

Endothermic: $\Delta H > 0$

Thermoneutral: $\Delta H = 0$

Enthalpy of Physical Changes

For phase transfers at constant pressure

Vaporization: $\Delta H_{vap} = H_{vapor} – H_{liquid}$

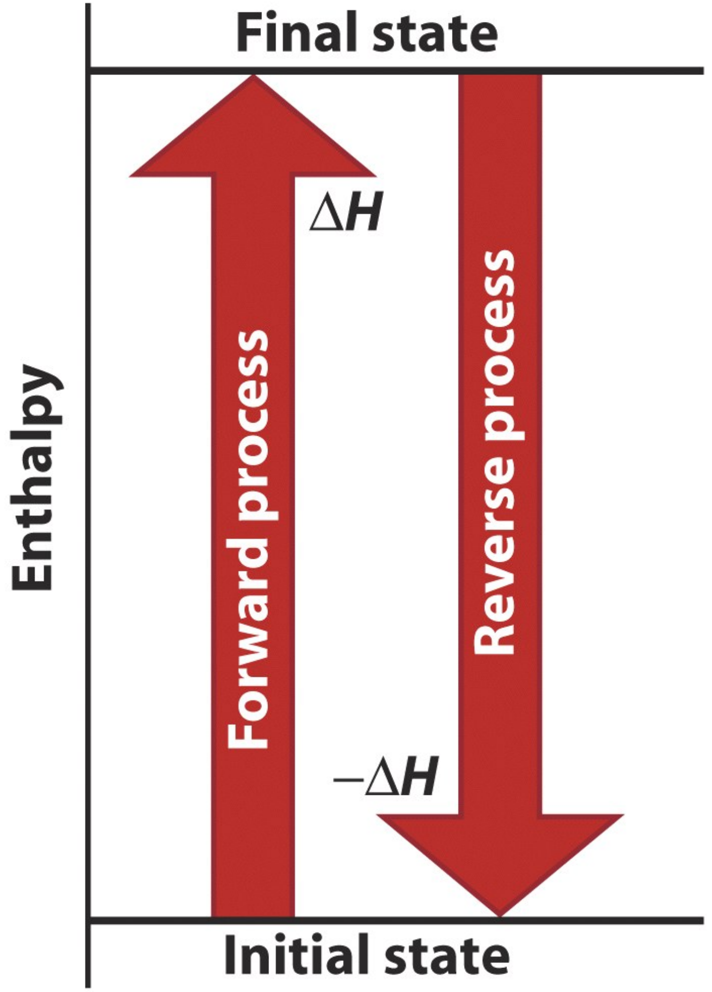
Melting (fusion): $\Delta H_{fus} = H_{liquid} – H_{solid}$

Sublimation: $\Delta H_{subl} = H_{vapor} – H_{solid}$

For the same temp: $\Delta H_{subl} = \Delta H_{vap} + H_{fus}$

$$\Delta H_{forward} = -\Delta H_{reverse}$$

Consequences of being a state function



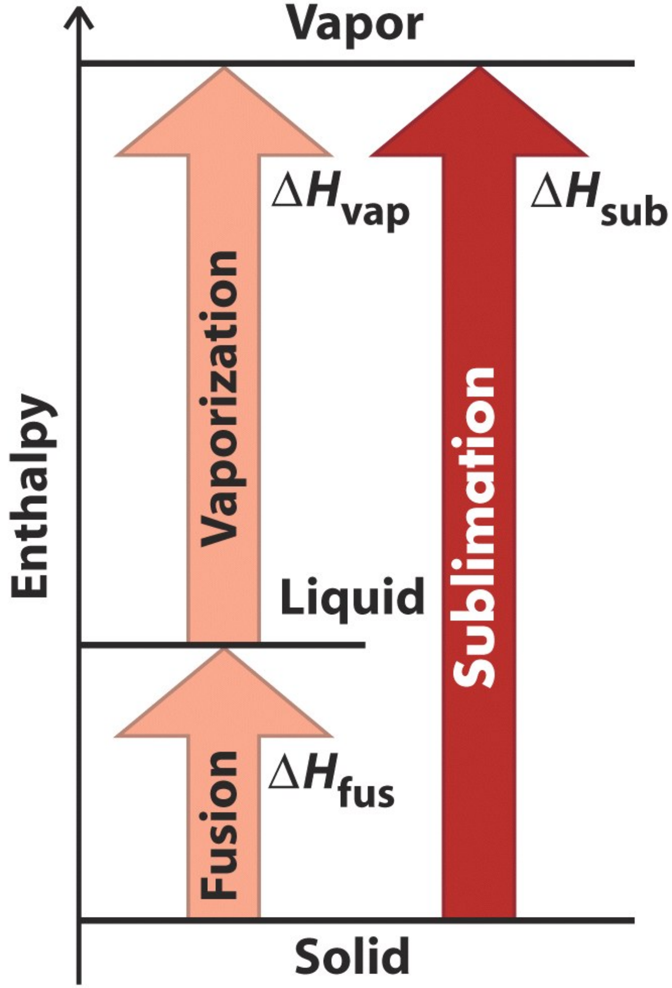


TABLE 7.3 Standard Enthalpies of Physical Change*

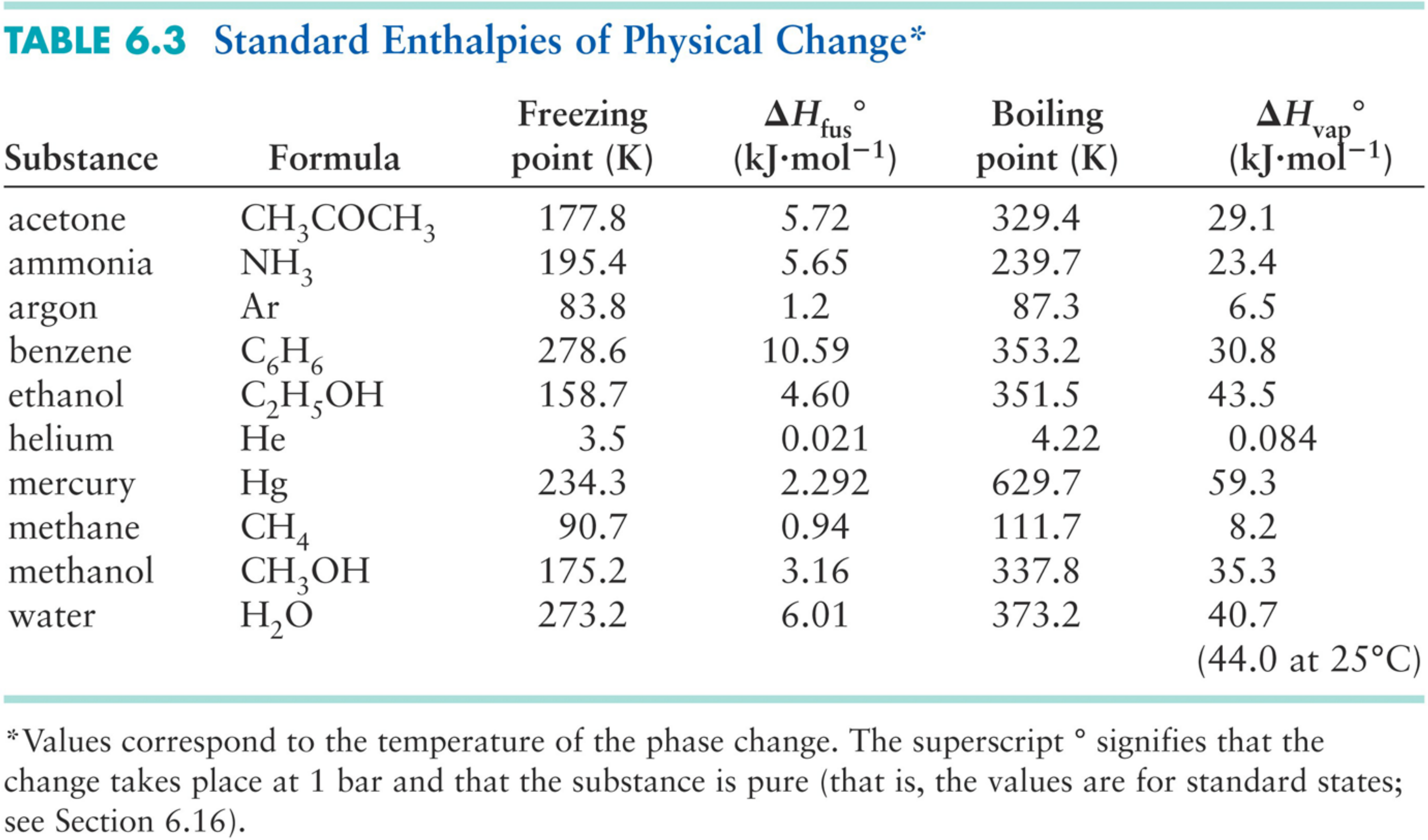
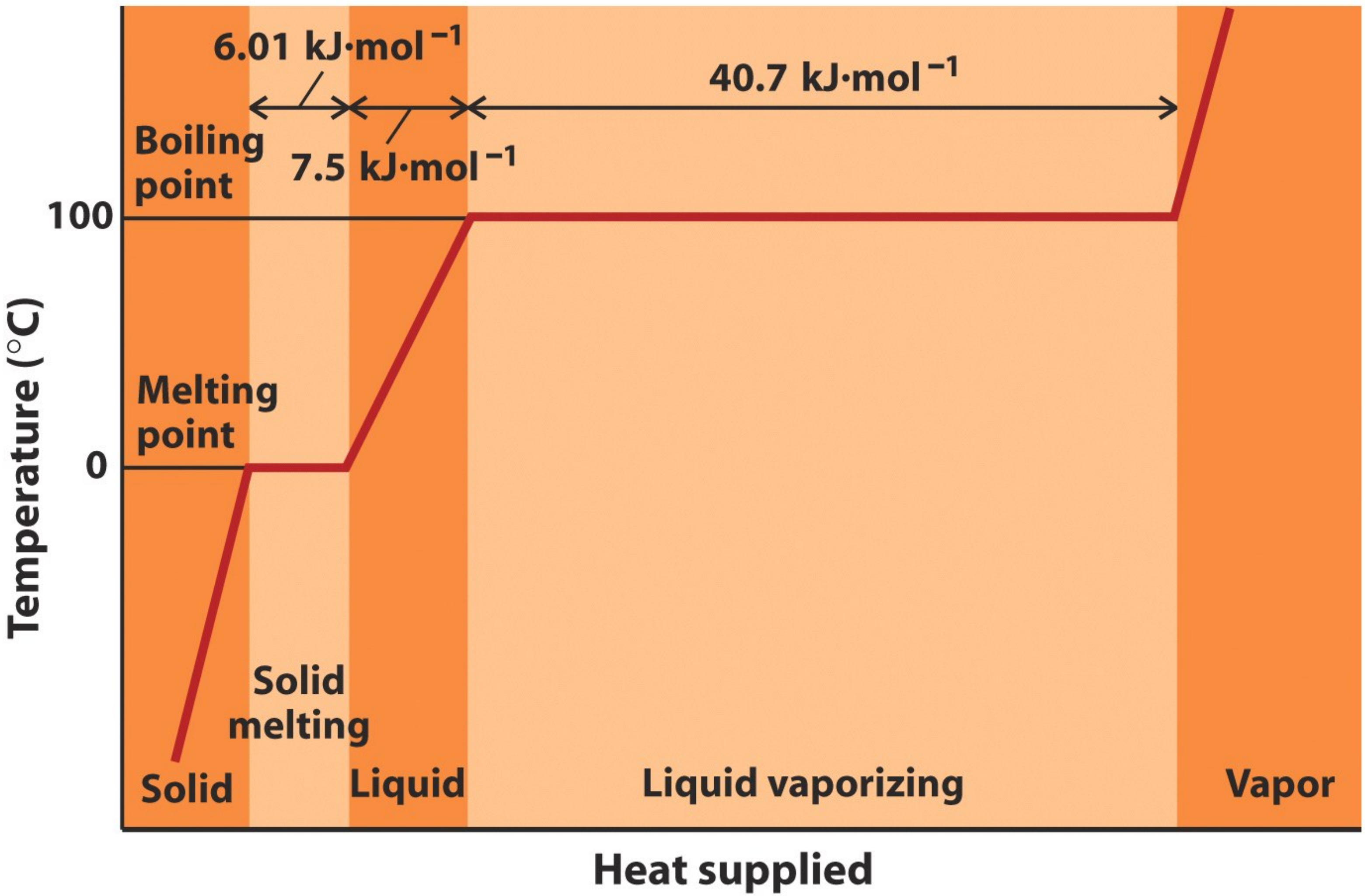


TABLE 6.3 Standard Enthalpies of Physical Change*

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 6.16).

Heating Curve



Enthalpy of chemical change (reaction)

Enthalpy of reaction is the heat released or absorbed as a result of a chemical reaction

$$\Delta H_{rxn} = \Sigma H_{products} - \Sigma H_{reactants}$$

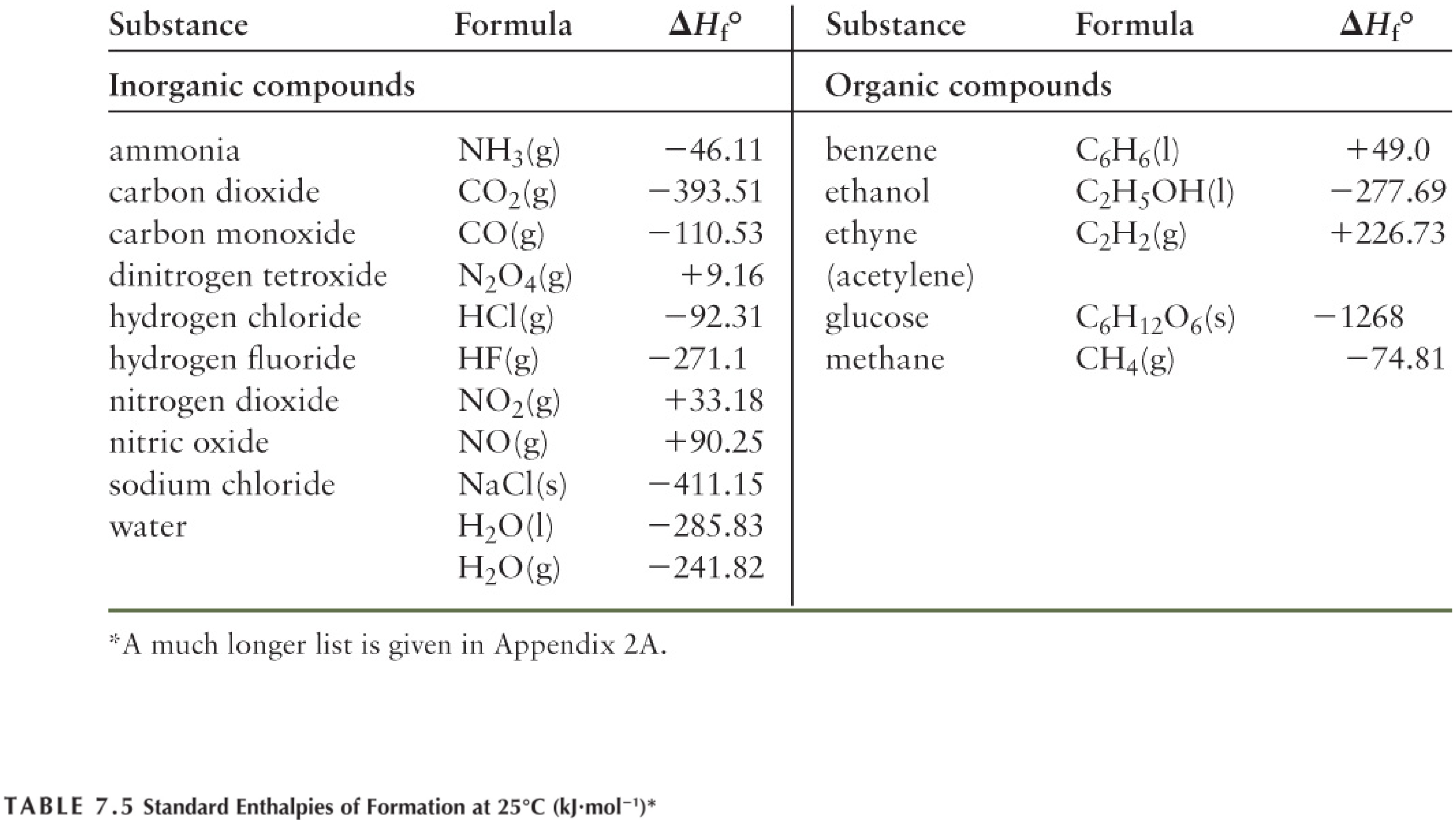
$$\Delta H_{rxn} = \Delta U_{rxn} + \Delta n_{gas}RT$$

Standard reaction enthalpy (ΔH^{o}) refers to reactions where all products and reactants are in their standard state

Definitions of Standard States

- For a gas the standard state is a pressure of exactly 1 atmosphere.
- For a substance present in a solution, the standard state is a concentration of exactly 1 *M*.
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For an element the standard state is the form in which the element exists under conditions of 1 atmosphere and 25 ^oC.

Standard Enthalpies of Formation



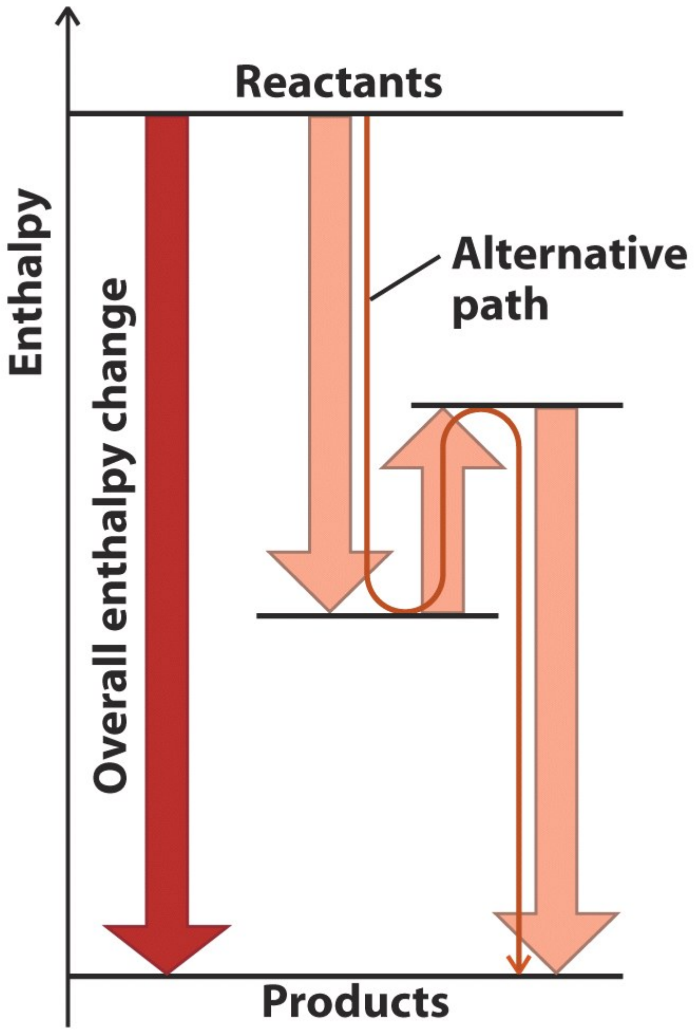
Substance	Formula	ΔH_f°	Substance	Formula	ΔH_f°
Inorganic compounds			**Organic compounds**		
ammonia	$NH_3(g)$	−46.11	benzene	$C_6H_6(l)$	+49.0
carbon dioxide	$CO_2(g)$	−393.51	ethanol	$C_2H_5OH(l)$	−277.69
carbon monoxide	$CO(g)$	−110.53	ethyne	$C_2H_2(g)$	+226.73
dinitrogen tetroxide	$N_2O_4(g)$	+9.16	(acetylene)		
hydrogen chloride	$HCl(g)$	−92.31	glucose	$C_6H_{12}O_6(s)$	−1268
hydrogen fluoride	$HF(g)$	−271.1	methane	$CH_4(g)$	−74.81
nitrogen dioxide	$NO_2(g)$	+33.18			
nitric oxide	$NO(g)$	+90.25			
sodium chloride	$NaCl(s)$	−411.15			
water	$H_2O(l)$	−285.83			
	$H_2O(g)$	−241.82			

*A much longer list is given in Appendix 2A.

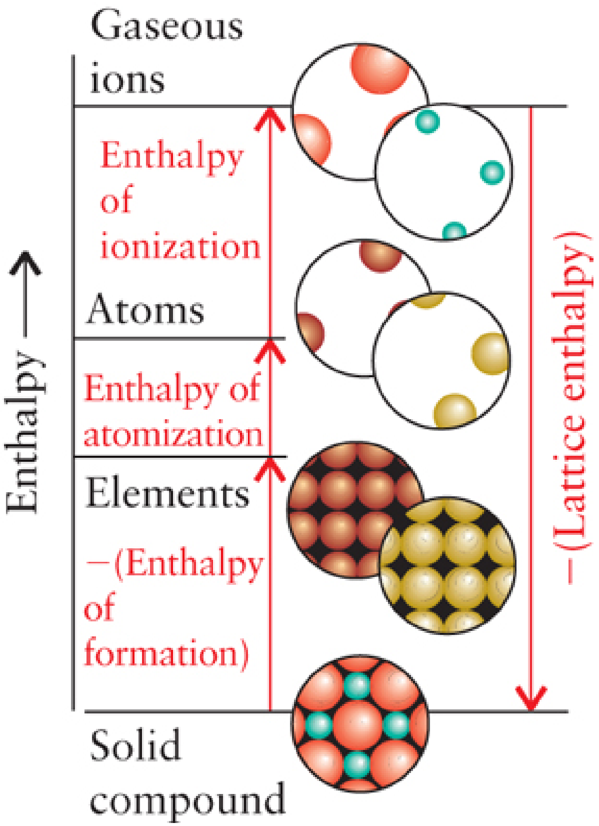
TABLE 7.5 **Standard Enthalpies of Formation at 25°C (kJ·mol^{-1})***

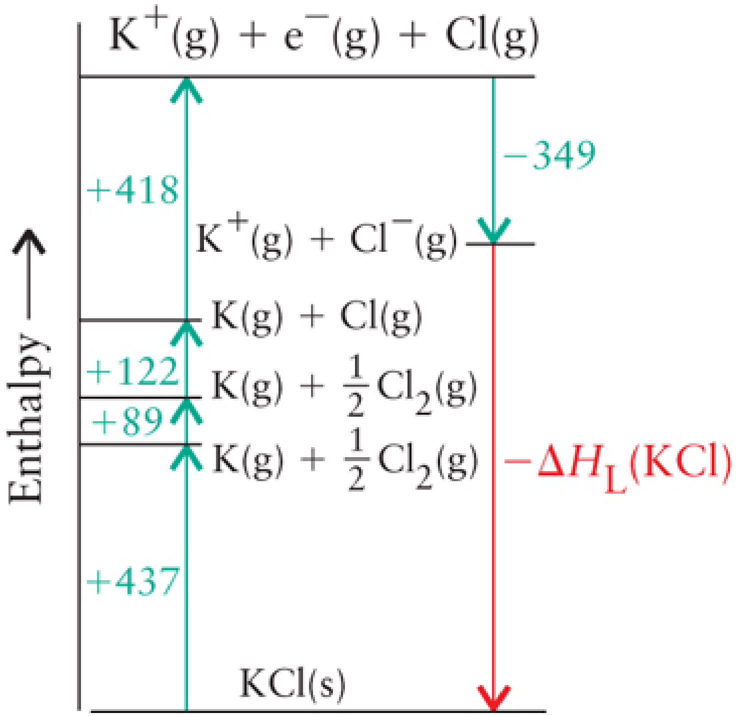
Hess’s law

The overall reaction enthalpy is the sum of the reaction enthalpies of the steps into which the reaction can be divided



Born-Haber cycle





An Application of Hess's Law:

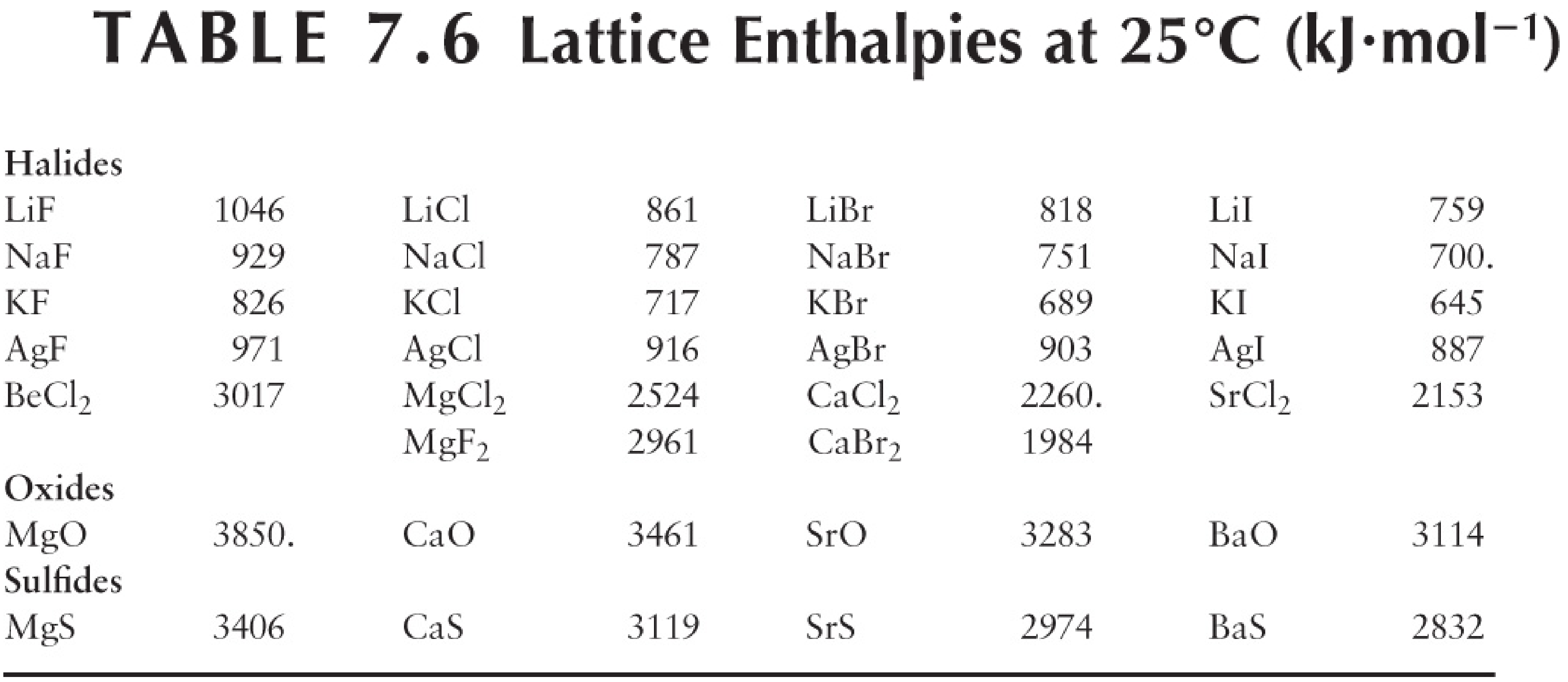
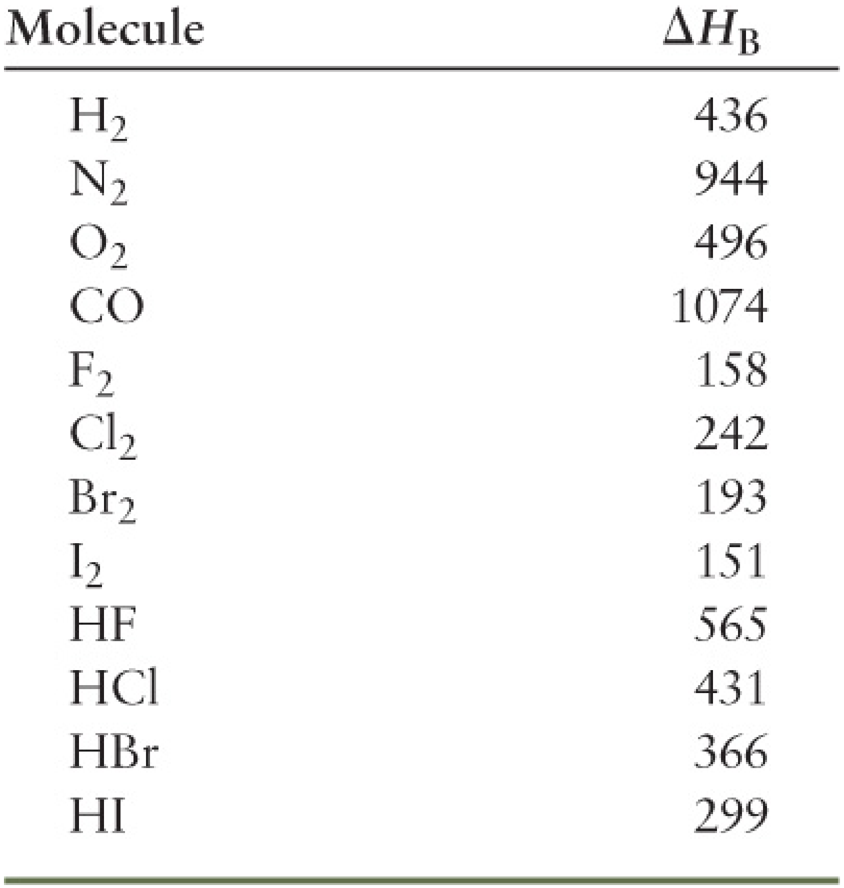


TABLE 7.6 Lattice Enthalpies at 25°C (kJ·mol^{-1})

Halides							
LiF	1046	LiCl	861	LiBr	818	LiI	759
NaF	929	NaCl	787	NaBr	751	NaI	700.
KF	826	KCl	717	KBr	689	KI	645
AgF	971	AgCl	916	AgBr	903	AgI	887
$BeCl_2$	3017	$MgCl_2$	2524	$CaCl_2$	2260.	$SrCl_2$	2153
		MgF_2	2961	$CaBr_2$	1984		
Oxides							
MgO	3850.	CaO	3461	SrO	3283	BaO	3114
Sulfides							
MgS	3406	CaS	3119	SrS	2974	BaS	2832

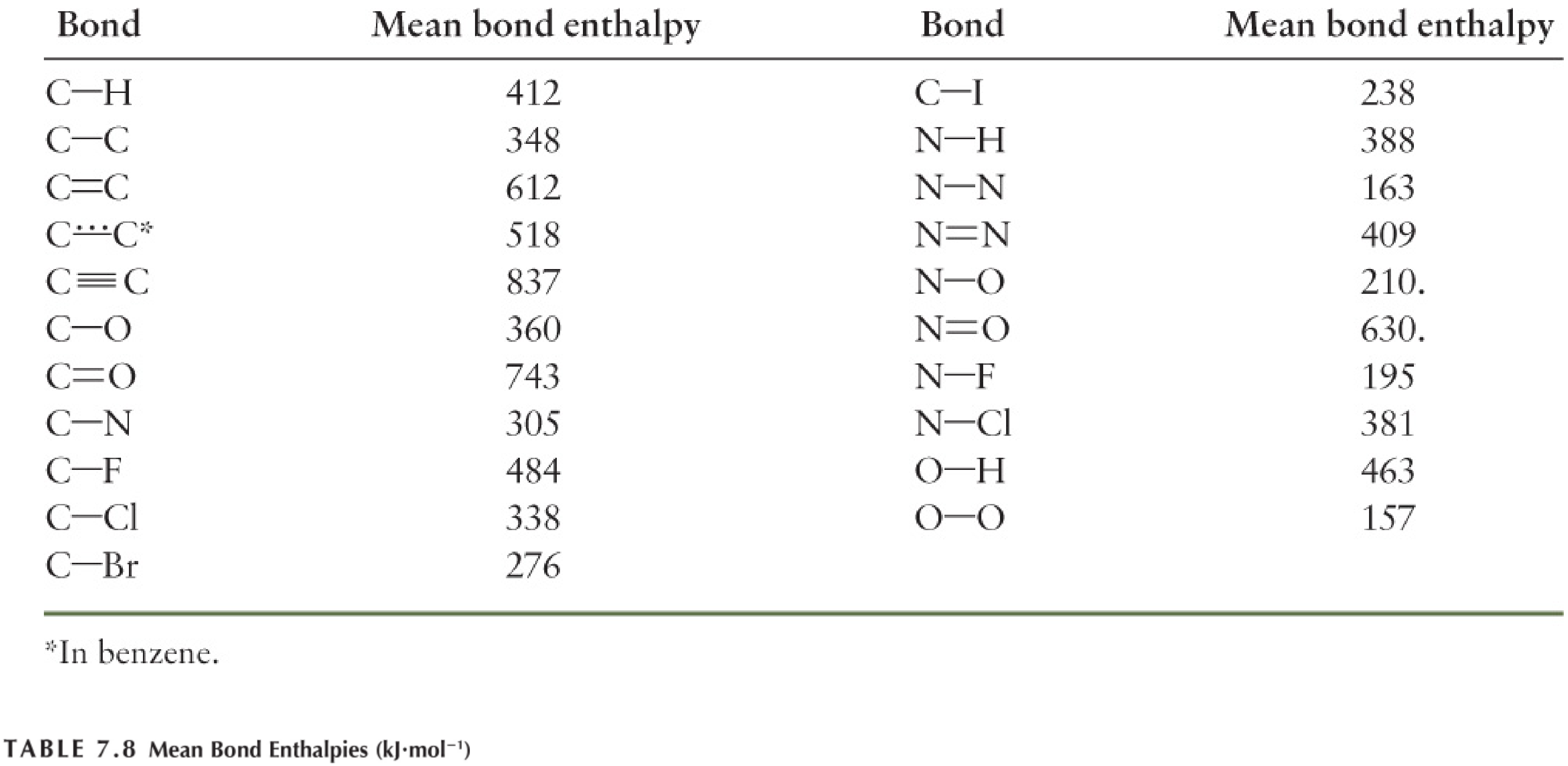
Bond Enthalpies of Diatomic Molecules



Molecule	ΔH_B
H_2	436
N_2	944
O_2	496
CO	1074
F_2	158
Cl_2	242
Br_2	193
I_2	151
HF	565
HCl	431
HBr	366
HI	299

TABLE 7.7 Bond Enthalpies of Diatomic Molecules ($kJ \cdot mol^{-1}$)

Average Bond Enthalpies in kJ/mol



Bond	Mean bond enthalpy	Bond	Mean bond enthalpy
$\mathrm{C-H}$	412	$\mathrm{C-I}$	238
$\mathrm{C-C}$	348	$\mathrm{N-H}$	388
$\mathrm{C=C}$	612	$\mathrm{N-N}$	163
$\mathrm{C\overset{\cdots}{-}C}$*	518	$\mathrm{N=N}$	409
$\mathrm{C\equiv C}$	837	$\mathrm{N-O}$	210.
$\mathrm{C-O}$	360	$\mathrm{N=O}$	630.
$\mathrm{C=O}$	743	$\mathrm{N-F}$	195
$\mathrm{C-N}$	305	$\mathrm{N-Cl}$	381
$\mathrm{C-F}$	484	$\mathrm{O-H}$	463
$\mathrm{C-Cl}$	338	$\mathrm{O-O}$	157
$\mathrm{C-Br}$	276		

*In benzene.

TABLE 7.8 **Mean Bond Enthalpies ($\mathrm{kJ \cdot mol^{-1}}$)**

ENTROPY

A *spontaneous* process has a tendency to occur without being driven by an external influence; does not have to be fast

Entropy is a measure of disorder (probability?)

Entropy is a state function

The 2nd law:

The entropy of an isolated system increases in the course of any spontaneous change

Changes in physical state and entropy (changes)

During the phase transition, the temperature remains constant

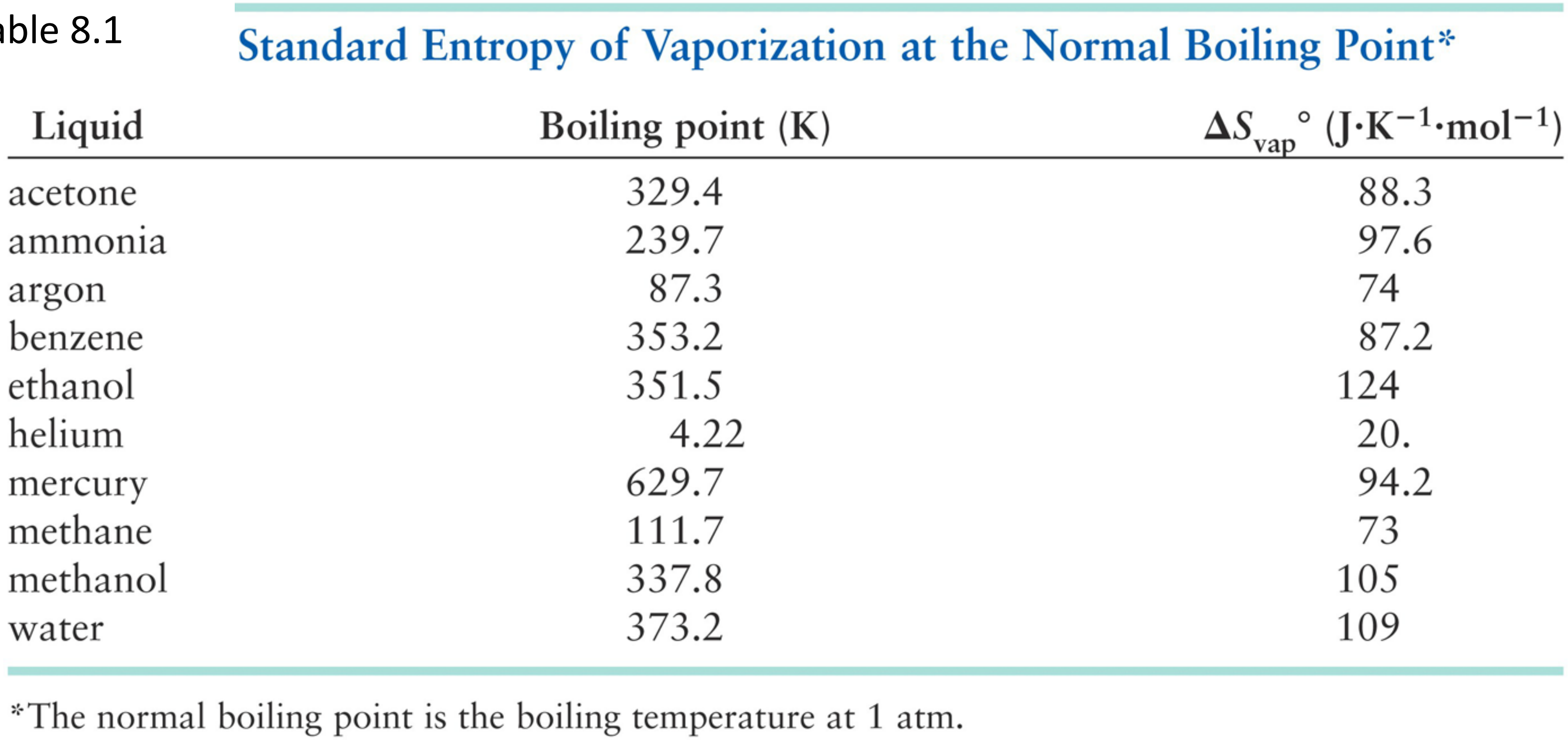
At the temperature of phase transition, the transfer of heat is reversible

For P = const, $q_{transition} = \Delta H_{transition}$

Ergo: $\Delta S_{transition} = \Delta H_{transition}/T_{transition}$

$\Delta S^0_{transition}$ – standard entropy of transition (J mol^{-1} K^{-1})

Table 8.1



Standard Entropy of Vaporization at the Normal Boiling Point*

Liquid	Boiling point (K)	$\Delta S_{\text{vap}}{}^{\circ}$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)
acetone	329.4	88.3
ammonia	239.7	97.6
argon	87.3	74
benzene	353.2	87.2
ethanol	351.5	124
helium	4.22	20.
mercury	629.7	94.2
methane	111.7	73
methanol	337.8	105
water	373.2	109

*The normal boiling point is the boiling temperature at 1 atm.

Entropy

The change in entropy is positive for melting, evaporation, and sublimation

Empirical Troutons “rule”: $\Delta S_{vap} \approx 85$ kJ/mol for many liquids

Calculating entropy of phase change at a different T?

- T of phase 1 is brought to the standard phase change T
- Phase 1 changes to phase 2 at standard phase change T
- T is brought back to the original T

The Third Law of Thermodynamics

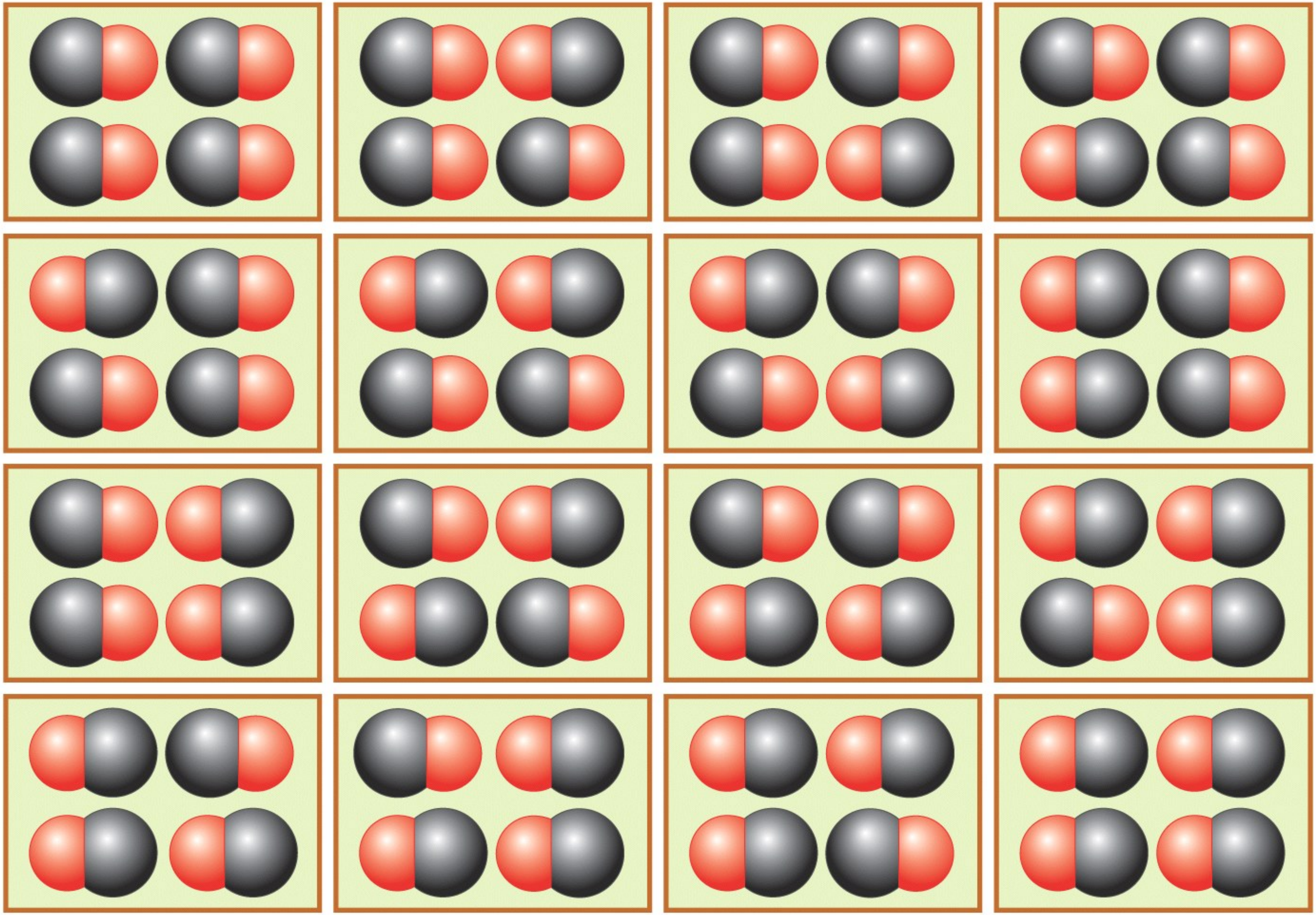
The entropies of all perfect crystals approach zero as the absolute temperature approaches zero

Statistical entropy

$S = k \ln(W)$,

where W is the number of different microstates for the macrostate

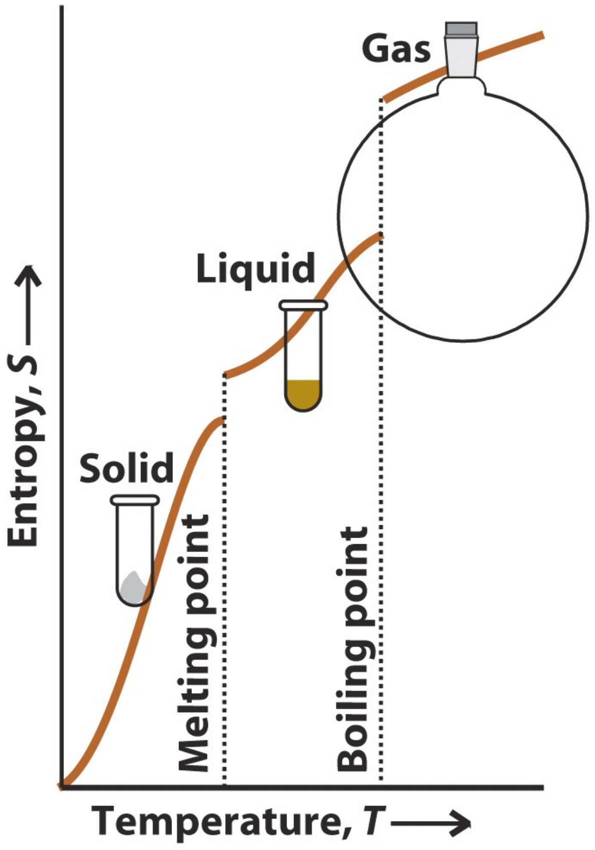
The statistical definition of entropy is equivalent to that derived from macroscopic observations

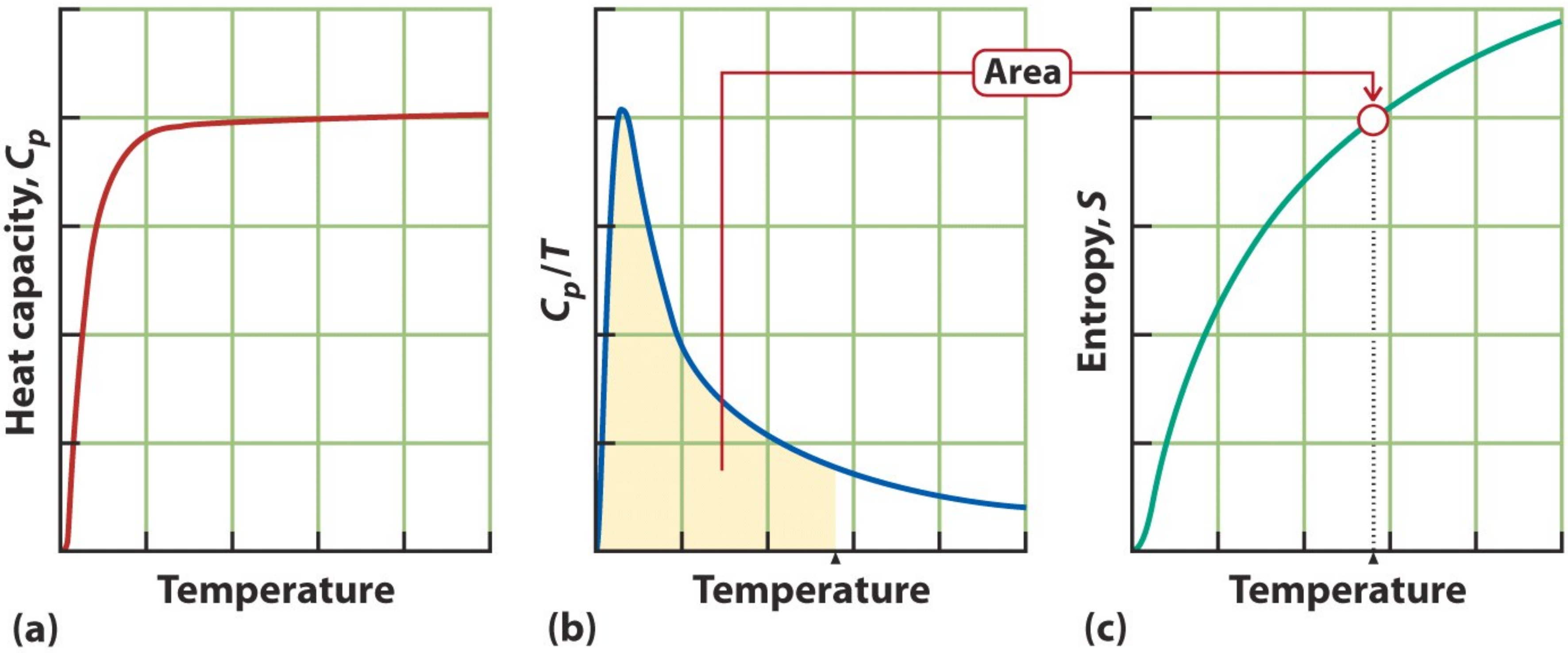


Standard molar entropy (S^0_m)

$S(T) = S(0) + \Delta S(0 \rightarrow T)$

$\Delta S(0 \rightarrow T)$ must account for phase transitions




Heat capacity, C_p
Temperature
(a)
C_p/T
Temperature
(b)
Area
Entropy, S
Temperature
(c)

Standard reaction entropy

$\Delta S^0_{rxn} = \Sigma n S^0_m(\text{products}) - \Sigma n S^0_m(\text{reactants})$

For reactions in which the amount of gas increases, ΔS^0_{rxn} is usually positive (and vice versa).

Also, generally, the increase in the number of particles in (ideal) solution or gas phase leads to increase in entropy.