

Chapter 18 Thermodynamics and Equilibrium

These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests!

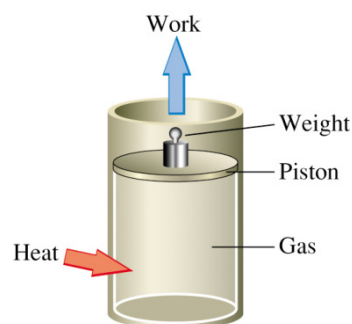
To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

18.1 First Law of Thermodynamics – Enthalpy. The change in internal energy of a system, $\Delta U = q + w$

Internal Energy: the sum of the Kinetic and Potential Energies of the particles making up a system

State Function: a property of a system that depends only on it's present state, which is determined by variables such as temperature and pressure

Work: energy exchange that results when a force F moves an object through a distance d ; $w = F * d$.



Take a cylinder with a piston with a weight on it. Add heat to the system, the pressure inside of the cylinder increases and this causes the piston to move up. Work is done in moving the piston up: work = Force * distance. The system gains energy by the heat absorbed, but loses some by the work done: $\Delta U = q + w$.

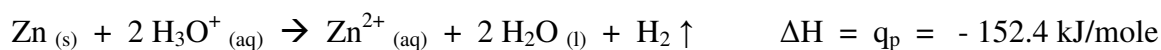
If the heat gained was + 165 J and the work done to move the piston up was - 92 J, minus because energy of the system was lost, then

$$\Delta U = q + w = (+165 \text{ J}) + (-92 \text{ J}) = +73 \text{ J} = \text{the change in internal}$$

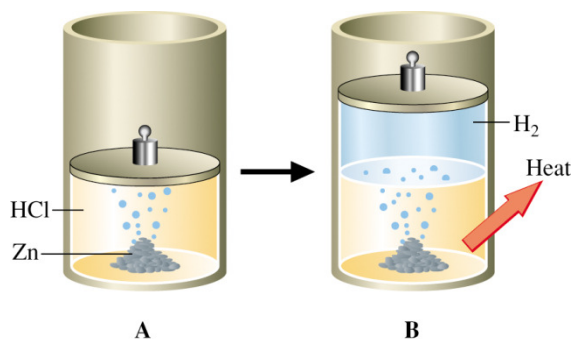
energy of the system

Exercise 18.1 In a similar system, the weight on the piston is 2.20 kg. The gas is now compressed and lowered 0.250 m. 1.50 J of heat is evolved. What is the change in internal energy of the system ΔU . The force of gravity on a mass m in mg is $g = 9.80 \text{ m/s}^2$.

Heats of Reaction and Internal Energy



q_p = heat evolved at constant pressure



The increase in volume due to H_2 is ΔV .

The change in volume is the height times area of the piston: $\Delta V = A * h$.

$$\text{Work} = w = -F * h = -F * \Delta V / A = (-F / A) * \Delta V \quad [\text{Force} / \text{Area} = \text{Pressure}]$$

$$w = -P \Delta V$$

From the above example, 1.00 mole Zn reacts with Xcs HCl to produce 1.00 mol H_2

At 25 °C, 1.00 atm [$1.01 \times 10^5 \text{ Pa}$], Volume = 24.5 L = $24.5 \times 10^{-3} \text{ m}^3$.

$$PV = nRT \quad V = n R T / P = \frac{1.00 \text{ mol} * 0.08205 \text{ L atm} / \text{mol K} * 298 \text{ K}}{1.00 \text{ atm}} = 25.45 = 25.5 \text{ L}$$

$$w = -P \Delta V = -(1.01 \times 10^5 \text{ Pa}) * (24.5 \times 10^{-3} \text{ m}^3) = -2.47 \times 10^3 \text{ J} = -2.47 \text{ kJ}$$

Note: 1 Pascal (Pa) = 1 kg/(ms²). 1 atm = $1.01325 \times 10^5 \text{ Pa}$

The Change in Internal Energy of the System:

$$\Delta U = q + w = -152.4 \text{ kJ} [\text{as heat given off}] - 2.47 \text{ kJ} [\text{as expansion work}] = 154.9 \text{ kJ}$$

Exercise 18.2: Methane is burned in excess oxygen to produce carbon dioxide and water. At 25 oC, 1.00 atm, $\Delta H = -890.2 \text{ kJ}$. What is w for this change?

Enthalpy

Enthalpy, H is the heat of reaction at constant pressure.

$$\Delta H = q$$

$$- \text{or} - \Delta H = \sum n \Delta H^{\circ}_f (\text{products}) - \sum n \Delta H^{\circ}_f (\text{reactants}) \quad [\text{Heat of formation products} - \text{reactants}]$$



$$\text{See Table Below:} \quad 2 \text{NH}_3_{(g)} = 2 * -45.90 \text{ kJ} \quad \text{CO}_2_{(g)} = -393.5 \text{ kJ}$$

$$\text{NH}_2\text{CONH}_2_{(aq)} = -319.2 \text{ kJ} \quad \text{H}_2\text{O}_{(l)} = -285.8 \text{ kJ}$$

$$\Delta H = [(-319.2 - 285.8) - (2 * -45.90 - 393.5)] \text{ kJ} = -119.7 \text{ kJ} \quad \text{Minus} = \text{Exothermic}$$

Spontaneous Process = The physical or chemical change occurs by itself

Rock rolls down a hill

Non-spontaneous – they do not occur by itself.

Rock rolls up a hill

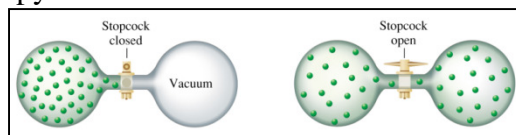
Entropy, S is a thermodynamic quantity that is a measure of how dispersed the energy of a system is among the different possible ways that a system can contain energy.

The Entropy (energy dispersal) of a system increases in a spontaneous process.

A hot cup of coffee on a table cools down as the energy is absorbed by its surroundings. Energy is dispersed.

A rock falls down a hill. Some Potential Energy is converted to Kinetic Energy, but also some is converted to bumping into the air molecules spreading out the energy. Energy is dispersed.

A gas is in one flask, which is connected to an empty flask. When the valve is opened, gas flows to the empty flask. The energy is dispersed, entropy is increased



Entropy is a state function, depends only on temp and pressure. **The SI units are J/K**

One mole of ice at 0° C, 1 atm $S = 41 \text{ J/K}$

One mole of water at 0° C, 1 atm, $S = 63 \text{ J/K}$

Change in Entropy = $\Delta S = S_{\text{final}} - S_{\text{initial}}$

For water/ice $\Delta S = S_{\text{ice}} - S_{\text{liquid}} = 63 \text{ J/K} - 41 \text{ J/K} = 22 \text{ J/K}$

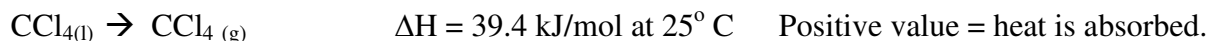
When ice melts, it increases in Entropy by 22 J/K

Second Law of Thermodynamics: The total entropy of a system and its surroundings always increases for a spontaneous process – or – For a spontaneous process at a given temperature, T, the change in entropy of the system is greater than the heat divided by the absolute temp – q / T .

The heat of fusion for ice \rightarrow water is $\Delta H = 6.0 \text{ kJ/mole}$ of ice.

$$\Delta S = q / T = 6,000 \text{ J} / 273 \text{ K} = 22 \text{ J/K}$$

Example 18.1 CCl_4 , $\Delta H_{\text{vap}} = 39.4 \text{ kJ/mol}$ at 25° C. If one mole of liquid CCl_4 has an Entropy of 216 J/K, what is the entropy of 1 mole of the vapor in equilibrium with the liquid.



$$\Delta S = q / T = 39,400 \text{ J} / 298 \text{ K} = 132 \text{ J/mol K}$$

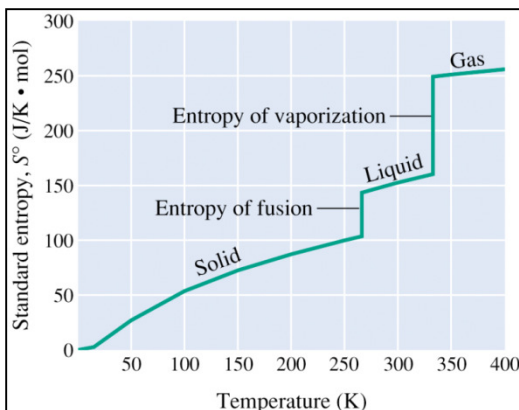
Entropy of CCl_4 increases by 132 J/mol K in going from liq to gas

$$\text{Entropy of } \text{CCl}_4 \text{ vapor} = 216 \text{ J/mol K} + 132 \text{ J/mol K} = 348 \text{ J/mol K}$$

Third Law of Thermodynamics: a substance that is perfectly crystalline at 0 K has entropy of zero.

	From	To	Heat Absorbed	$\Delta S = \Delta H / T$
Heat Some Stuff	0.0 K	2.0 K	0.19 J	0.19 J/K
	2.0 K	4.0 K	0.88 J	0.29 J/K

The Entropy at 4.0 K = 0.19 J/K + 0.29 J/K = 0.48 J/K



Entropy of Bromine vs increase in Temp. Sharp jumps

are at the phase changes.

Standard Entropy = Absolute Entropy = S° is the entropy value for the standard state of the substance, 1 atm, 1 M, 25 °C.

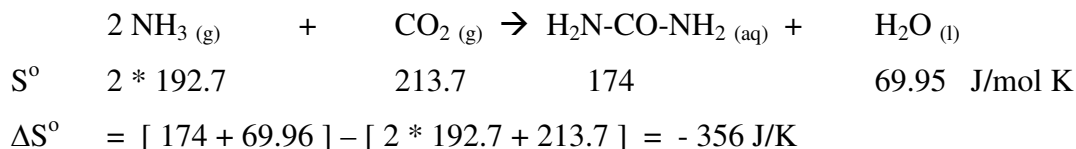
Entropy Change for a Reaction See table 18.1 below

Entropy usually increases when:

1. One molecule is broken into two or more smaller molecules
2. There is an increase in the moles of gas produced
3. A solid \rightarrow liquid, liquid \rightarrow gas

For semi-quantative work, you can **calculate ΔS° from $\Delta S^\circ = \sum n\Delta S^\circ_{(\text{products})} - \sum n\Delta S^\circ_{(\text{reactants})}$**

Example 18.3 Ammonia and Carbon Dioxide react to form Urea at 25 °C. Urea S° is 174 J/mK. What is ΔS° ?



Note the moles of gas decrease, so we expect the entropy to decrease.

If $\Delta H^\circ - T \Delta S^\circ$ is negative, the reaction is spontaneous, if positive the reaction is non-spontaneous, if zero, the reaction is at equilibrium.

$$\Delta H^\circ - T \Delta S^\circ = - 119.7 \text{ kJ} - (298 \text{ K} * 0.356 \text{ kJ/K}) = - 13.6 \text{ kJ. This reaction is spontaneous}$$

Gibbs Free Energy $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

The standard states for ΔG° is 1 atm pressure, 1 M concentration, and $T = 25^\circ \text{C}$ or 298 K.

Example 18.4 What is ΔG° for nitrogen and hydrogen reacting at 25°C to form ammonia.

	$\text{N}_2 (\text{g})$	+	$3 \text{H}_2 (\text{g})$	\rightarrow	$2 \text{NH}_3 (\text{g})$	
ΔH°	0		0		-45.90 kJ/M	Std Enthalpies of Formation Table 6.2
ΔS°	191.6		$3 * 130.6$		$2 * 192.7 \text{ J/K}$	Standard Entropies Table 18.1

$$\Delta H^\circ = \sum n\Delta H^\circ_{(\text{products})} - \sum n\Delta H^\circ_{(\text{reactants})} = [2 * -45.90] - 0 = -91.8 \text{ kJ}$$

$$\Delta S^\circ = \sum n\Delta S^\circ_{(\text{products})} - \sum n\Delta S^\circ_{(\text{reactants})} = [2 * 192.7] \text{ J/K} - [191.6 + 3 * 130.6] \text{ J/K} = -198.0 \text{ J/K}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -91.8 \text{ kJ} - [298 \text{ K} * -0.1980 \text{ kJ/K}] = -32.8 \text{ kJ}$$

ΔG°_f is the **Standard Free Energy of Formation** = the free energy change that occurs when 1 mole of substance is formed from its elements in their stablest states at 1 atm and $T = 25^\circ \text{C}$.

$$\Delta G^\circ = \sum n\Delta G^\circ_F (\text{products}) - \sum n\Delta G^\circ_F (\text{reactants}) = \text{See Table 18.2}$$

If ΔG° is more negative than -10 kJ Reaction is spontaneous

If ΔG° is more positive than +10 kJ Reaction is NON-spontaneous

If ΔG° is small negative or positive Reaction is an equilibrium mixture

Example 18.6

Exercise 18.8

Coupling Reactions Rust \rightarrow Iron

Free Energy Change during a reaction

Free Energy Change & Equilibrium Constants

$$\Delta G^\circ = -RT \ln K$$

Where K is the Thermodynamic Equilibrium Constant – concentration of gases are expressed as partial pressures in atm, solutions as M.

ΔH_f Heat of Reaction at Constant Pressure

TABLE 6.2 Standard Enthalpies of Formation (at 25°C)*					
Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)
$e^-(g)$	0	$CH_3CHO(g)$	-166.1	$NO_2(g)$	33.10
Bromine		$CH_3CHO(l)$	-191.8	$HNO_3(aq)$	-207.4
$Br(g)$	111.9	Chlorine		Oxygen	
$Br^-(aq)$	-121.5	$Cl(g)$	121.3	$O(g)$	249.2
$Br^-(g)$	-219.0	$Cl^-(aq)$	-167.2	$O_2(g)$	0
$Br_2(g)$	30.91	$Cl^-(g)$	-234.0	$O_3(g)$	142.7
$Br_2(l)$	0	$Cl_2(g)$	0	$OH^-(aq)$	-230.0
$HBr(g)$	-36.44	$HCl(g)$	-92.31	$H_2O(g)$	-241.8
Calcium		Fluorine		$H_2O(l)$	-285.8
$Ca(s)$	0	$F(g)$	79.39	Silicon	
$Ca^{2+}(aq)$	-542.8	$F^-(g)$	-255.1	$Si(s)$	0
$CaCO_3(s, \text{ calcite})$	-1206.9	$F^-(aq)$	-332.6	$SiCl_4(l)$	-687.0
$CaO(s)$	-635.1	$F_2(g)$	0	$SiF_4(g)$	-1614.9
Carbon		$HF(g)$	-272.5	$SiO_2(s, \text{ quartz})$	-910.9
$C(g)$	716.7	Hydrogen		Silver	
$C(s, \text{ diamond})$	1.897	$H(g)$	218.0	$Ag(s)$	0
$C(s, \text{ graphite})$	0	$H^+(aq)$	0	$Ag^+(aq)$	105.6
$CCl_4(g)$	-95.98	$H^+(g)$	1536.2	$AgBr(s)$	-100.4
$CCl_4(l)$	-135.4	$H_2(g)$	0	$AgCl(s)$	-127.1
$CO(g)$	-110.5	Iodine		$AgF(s)$	-204.6
$CO_2(g)$	-393.5	$I(g)$	106.8	$AgI(s)$	-61.84
$CO_3^{2-}(aq)$	-677.1	$I^-(aq)$	-55.19	Sodium	
$CS_2(g)$	116.9	$I^-(g)$	-194.6	$Na(g)$	107.3
$CS_2(l)$	89.70	$I_2(s)$	0	$Na(s)$	0
$HCN(g)$	135.1	$HI(g)$	26.36	$Na^+(aq)$	-240.1
$HCN(l)$	108.9	Lead		$Na^+(g)$	609.3
$HCO_3^-(aq)$	-692.0	$Pb(s)$	0	$Na_2CO_3(s)$	-1130.8
<i>Hydrocarbons</i>		$Pb^{2+}(aq)$	-1.7	$NaCl(s)$	-411.1
$CH_4(g)$	-74.87	$PbO(s)$	-219.4	$NaHCO_3(s)$	-950.8
$C_2H_4(g)$	52.47	$PbS(s)$	-98.32	Sulfur	
$C_2H_6(g)$	-84.68	Nitrogen		$S(g)$	277.0
$C_6H_6(l)$	49.0	$N(g)$	472.7	$S(s, \text{ monoclinic})$	0.360
<i>Alcohols</i>		$N_2(g)$	0	$S(s, \text{ rhombic})$	0
$CH_3OH(l)$	-238.7	$NH_3(g)$	-45.90	$S_2(g)$	128.6
$C_2H_5OH(l)$	-277.7	$NH_4^+(aq)$	-132.5	$SO_2(g)$	-296.8
<i>Aldehydes</i>		$NO(g)$	90.29	$H_2S(g)$	-20.50
$HCHO(g)$	-117				

*See Appendix C for additional values.

S° Degree of “Disorder”

TABLE 18.1		Standard Entropies (at 25°C)*			
Substance or Ion	S _f [°] J/(mol·K)	Substance or Ion	S _f [°] J/(mol·K)	Substance or Ion	S _f [°] J/(mol·K)
e ⁻ (g)	20.87	<i>Aldehydes (continued)</i>		Nitrogen (continued)	
Bromine		CH ₃ CHO(g)	246.4	NO ₂ (g)	239.9
Br(g)	174.9	CH ₃ CHO(l)	160.4	HNO ₃ (aq)	146.4
Br ⁻ (aq)	82.4	Chlorine		Oxygen	
Br ⁻ (g)	163.4	Cl(g)	165.1	O(g)	160.9
Br ₂ (g)	245.3	Cl ⁻ (aq)	56.5	O ₂ (g)	205.0
Br ₂ (l)	152.2	Cl ⁻ (g)	153.2	O ₃ (g)	238.8
HBr(g)	198.6	Cl ₂ (g)	223.0	OH ⁻ (aq)	-10.75
Calcium		HCl(g)	186.8	H ₂ O(g)	188.7
Ca(s)	41.59	Fluorine		H ₂ O(l)	69.95
Ca ²⁺ (aq)	-53.1	F(g)	158.6	Silicon	
CaCO ₃ (s, calcite)	92.9	F ⁻ (g)	145.5	Si(s)	18.82
CaO(s)	38.21	F ⁻ (aq)	-13.8	SiCl ₄ (l)	239.7
Carbon		F ₂ (g)	202.7	SiF ₄ (g)	282.7
C(g)	158.0	HF(g)	173.7	SiO ₂ (s, quartz)	41.46
C(s, diamond)	2.377	Hydrogen		Silver	
C(s, graphite)	5.740	H(g)	114.6	Ag(s)	42.55
CCl ₄ (g)	309.7	H ⁺ (aq)	0	Ag ⁺ (aq)	72.68
CCl ₄ (l)	216.4	H ⁺ (g)	108.8	AgBr(s)	107.1
CO(g)	197.5	H ₂ (g)	130.6	AgCl(s)	96.2
CO ₂ (g)	213.7	Iodine		AgF(s)	83.7
CO ₃ ²⁻ (aq)	-56.9	I(g)	180.7	AgI(s)	115.5
CS ₂ (g)	237.9	I ⁻ (aq)	109.6	Sodium	
CS ₂ (l)	151.3	I ⁻ (g)	169.2	Na(g)	153.6
HCN(g)	201.7	I ₂ (s)	116.1	Na(s)	51.46
HCN(l)	112.8	HI(g)	206.5	Na ⁺ (aq)	59.1
HCO ₃ ⁻ (aq)	91.2	Lead		Na ⁺ (g)	147.8
<i>Hydrocarbons</i>		Pb(s)	64.78	Na ₂ CO ₃ (s)	138.8
CH ₄ (g)	186.1	Pb ²⁺ (aq)	10.5	NaCl(s)	72.12
C ₂ H ₄ (g)	219.2	PbO(s)	66.32	NaHCO ₃ (s)	101.7
C ₂ H ₆ (g)	229.5	PbS(s)	91.34	Sulfur	
C ₆ H ₆ (l)	173.4	Nitrogen		S(g)	167.7
<i>Alcohols</i>		N(g)	153.2	S(s, monoclinic)	33.03
CH ₃ OH(l)	126.8	N ₂ (g)	191.6	S(s, rhombic)	32.06
C ₂ H ₅ OH(l)	160.7	NH ₃ (g)	192.7	S ₂ (g)	228.1
<i>Aldehydes</i>		NH ₄ ⁺ (aq)	113.4	SO ₂ (g)	248.1
HCHO(g)	219.0	NO(g)	210.6	H ₂ S(g)	205.6

*See Appendix C for additional values.

ΔG_f° The Standard Free Energy of Formation

TABLE 18.2		Standard Free Energies of Formation (at 25°C)*			
Substance or Ion	ΔG_f° (kJ/mol)	Substance or Ion	ΔG_f° (kJ/mol)	Substance or Ion	ΔG_f° (kJ/mol)
$e^-(g)$	0	<i>Aldehydes (continued)</i>		Nitrogen (continued)	
Bromine		$CH_3CHO(l)$	-128.3	$HNO_3(aq)$	-111.3
$Br(g)$	82.40	Chlorine		Oxygen	
$Br^-(aq)$	-104.0	$Cl(g)$	105.3	$O(g)$	231.8
$Br^-(g)$	-238.8	$Cl^-(aq)$	-131.3	$O_2(g)$	0
$Br_2(g)$	3.159	$Cl^-(g)$	-240.2	$O_3(g)$	163.2
$Br_2(l)$	0	$Cl_2(g)$	0	$OH^-(aq)$	-157.3
$HBr(g)$	-53.50	$HCl(g)$	-95.30	$H_2O(g)$	-228.6
Calcium		Fluorine		$H_2O(l)$	-237.1
$Ca(s)$	0	$F(g)$	62.31	Silicon	
$Ca^{2+}(aq)$	-553.5	$F^-(g)$	-262.0	$Si(s)$	0
$CaCO_3(s, \text{ calcite})$	-1128.8	$F^-(aq)$	-278.8	$SiCl_4(l)$	-619.9
$CaO(s)$	-603.5	$F_2(g)$	0	$SiF_4(g)$	-1572.7
Carbon		$HF(g)$	-274.6	$SiO_2(s, \text{ quartz})$	-856.4
$C(g)$	671.3	Hydrogen		Silver	
$C(s, \text{ diamond})$	2.900	$H(g)$	203.3	$Ag(s)$	0
$C(s, \text{ graphite})$	0	$H^+(aq)$	0	$Ag^+(aq)$	77.12
$CCl_4(g)$	-53.65	$H^+(g)$	1517.0	$AgBr(s)$	-96.90
$CCl_4(l)$	-65.27	$H_2(g)$	0	$AgCl(s)$	-109.8
$CO(g)$	-137.2	Iodine		$AgF(s)$	—
$CO_2(g)$	-394.4	$I(g)$	70.21	$AgI(s)$	-66.19
$CO_3^{2-}(aq)$	-527.9	$I^-(aq)$	-51.59	Sodium	
$CS_2(g)$	66.85	$I^-(g)$	-221.5	$Na(g)$	76.86
$CS_2(l)$	65.27	$I_2(s)$	0	$Na(s)$	0
$HCN(g)$	124.7	$HI(g)$	1.576	$Na^+(aq)$	-261.9
$HCN(l)$	124.9	Lead		$Na^+(g)$	574.4
$HCO_3^-(aq)$	-586.8	$Pb(s)$	0	$Na_2CO_3(s)$	-1048.0
<i>Hydrocarbons</i>		$Pb^{2+}(aq)$	-24.39	$NaCl(s)$	-384.0
$CH_4(g)$	-50.80	$PbO(s)$	-189.3	$NaHCO_3(s)$	-851.0
$C_2H_4(g)$	68.39	$PbS(s)$	-96.68	Sulfur	
$C_2H_6(g)$	-32.89	Nitrogen		$S(g)$	236.5
$C_6H_6(l)$	124.4	$N(g)$	455.6	$S(s, \text{ monoclinic})$	0.070
<i>Alcohols</i>		$N_2(g)$	0	$S(s, \text{ rhombic})$	0
$CH_3OH(l)$	-166.4	$NH_3(g)$	-16.40	$S_2(g)$	79.7
$C_2H_5OH(l)$	-174.9	$NH_4^+(aq)$	-79.37	$SO_2(g)$	-300.1
<i>Aldehydes</i>		$NO(g)$	86.60	$H_2S(g)$	-33.33
$HCHO(g)$	-113	$NO_2(g)$	51.24		
$CH_3CHO(g)$	-133.4				

*See Appendix C for additional values.

Summary of Equations

change in internal energy of the system

$$\Delta U = q + w$$

Work done

$$w = -P \Delta V$$