PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

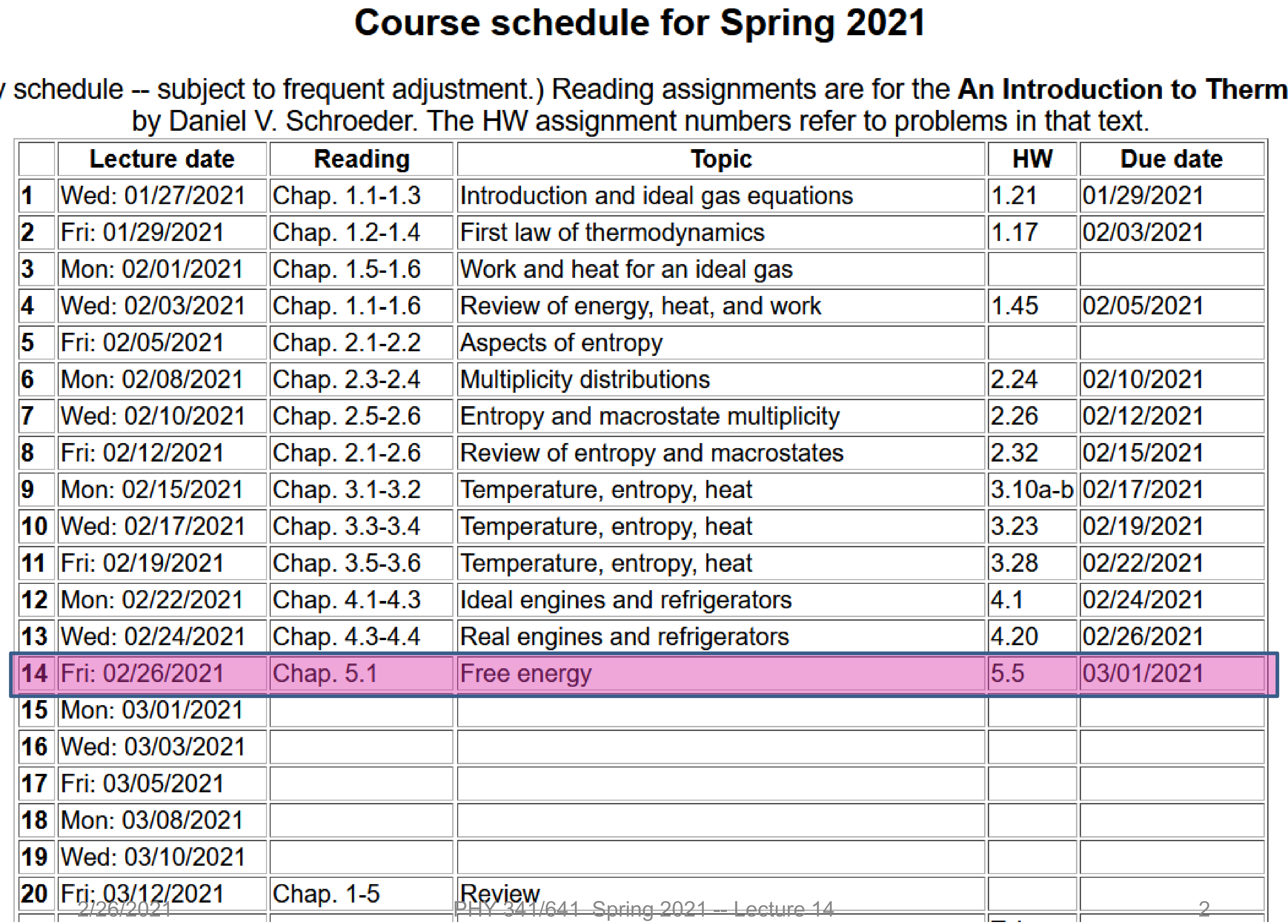
Record!!!

Discussion for Lecture 14:

Useful thermodynamic energy functions

Reading: Chapters 5.1

1. **Internal energy U**
2. **Enthalpy H**
3. **Helmholtz free energy F**
4. **Gibbs free energy G**



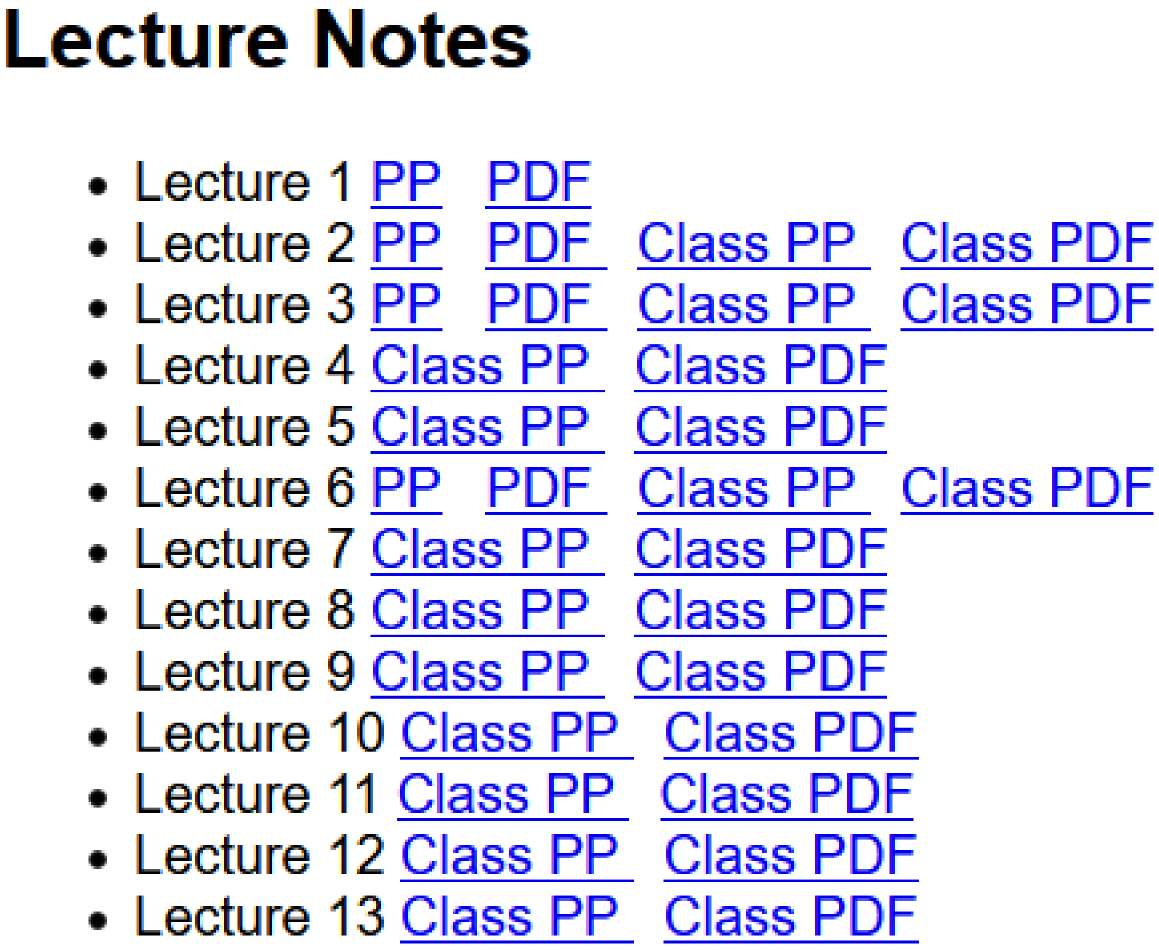
Course schedule for Spring 2021

schedule -- subject to frequent adjustment.) Reading assignments are for the **An Introduction to Therm**
by Daniel V. Schroeder. The HW assignment numbers refer to problems in that text.

	Lecture date	Reading	Topic	HW	Due date
1	Wed: 01/27/2021	Chap. 1.1-1.3	Introduction and ideal gas equations	1.21	01/29/2021
2	Fri: 01/29/2021	Chap. 1.2-1.4	First law of thermodynamics	1.17	02/03/2021
3	Mon: 02/01/2021	Chap. 1.5-1.6	Work and heat for an ideal gas		
4	Wed: 02/03/2021	Chap. 1.1-1.6	Review of energy, heat, and work	1.45	02/05/2021
5	Fri: 02/05/2021	Chap. 2.1-2.2	Aspects of entropy		
6	Mon: 02/08/2021	Chap. 2.3-2.4	Multiplicity distributions	2.24	02/10/2021
7	Wed: 02/10/2021	Chap. 2.5-2.6	Entropy and macrostate multiplicity	2.26	02/12/2021
8	Fri: 02/12/2021	Chap. 2.1-2.6	Review of entropy and macrostates	2.32	02/15/2021
9	Mon: 02/15/2021	Chap. 3.1-3.2	Temperature, entropy, heat	3.10a-b	02/17/2021
10	Wed: 02/17/2021	Chap. 3.3-3.4	Temperature, entropy, heat	3.23	02/19/2021
11	Fri: 02/19/2021	Chap. 3.5-3.6	Temperature, entropy, heat	3.28	02/22/2021
12	Mon: 02/22/2021	Chap. 4.1-4.3	Ideal engines and refrigerators	4.1	02/24/2021
13	Wed: 02/24/2021	Chap. 4.3-4.4	Real engines and refrigerators	4.20	02/26/2021
14	Fri: 02/26/2021	Chap. 5.1	Free energy	5.5	03/01/2021
15	Mon: 03/01/2021				
16	Wed: 03/03/2021				
17	Fri: 03/05/2021				
18	Mon: 03/08/2021				
19	Wed: 03/10/2021				
20	Fri: 03/12/2021	Chap. 1-5	Review		

Reminder – lecture notes are available on the class webpage

http://users.wfu.edu/natalie/s21phy341/lecturenote/



Lecture Notes

- Lecture 1 PP PDF
- Lecture 2 PP PDF Class PP Class PDF
- Lecture 3 PP PDF Class PP Class PDF
- Lecture 4 Class PP Class PDF
- Lecture 5 Class PP Class PDF
- Lecture 6 PP PDF Class PP Class PDF
- Lecture 7 Class PP Class PDF
- Lecture 8 Class PP Class PDF
- Lecture 9 Class PP Class PDF
- Lecture 10 Class PP Class PDF
- Lecture 11 Class PP Class PDF
- Lecture 12 Class PP Class PDF
- Lecture 13 Class PP Class PDF

Your questions –

From Kristen – 1. For the heat that is free from the environment, as in Helmholtz free energy, if there is indefinite heat, will it absorb all of the energy it needs from this or will we still have to input some work? 2. Could we review a bit about the reaction for the battery as discussed on page 154, I just need a bit of clarification.

From Parker -- We will invoke the Legendre transformation mathematically for changes in V to P and TS from S to T in this class?

From Michael -- Can you further explain why fuel cell engines are not more abundant in production given their high efficiency?

From Rich – In the Gibbs Free energy equation, how can the change in entropy be negative without violating the second law of thermodynamics?

From Noah -- Can you explain more why a problem would or would not care about the +PV term? E.g. why does the example of electrolysis use Gibbs free energy instead of Helmholtz?

Internal energy U

First law of thermodynamics

$$dU = Q + W$$

$$dU = TdS - PdV$$

$$Q \Leftrightarrow TdS \qquad\qquad W \Leftrightarrow -PdV$$

Note that this analysis implies that we should consider the internal energy

$$U = U(S,V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - PdV$$

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

Mathematical consistency

Suppose $f(x,y)$ such that $df = a(x,y)dx + b(x,y)dy$

$$\text{where } a(x,y) = \left(\frac{\partial f}{\partial x}\right)_y \quad \text{and} \quad b(x,y) = \left(\frac{\partial f}{\partial y}\right)_x$$

Check that second derivatives are consistent --

$$\frac{\partial^2 f}{\partial y \partial x} \equiv \frac{\partial}{\partial y}\left(\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \frac{\partial^2 f}{\partial x \partial y} \qquad \Rightarrow \left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y$$

Maxwell’s relations

For example: $U = U(S,V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - PdV$$

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

Maxwell's relations show that

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

Generalizing U to allow for variable N --

Are these equation internally consistent?

$$dU = TdS - PdV + \mu dN$$

Suppose U and V are constant; $dU = 0$ and $dV = 0$

$$\Rightarrow 0 = TdS - 0 + \mu dN$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Suppose S and V are constant; $dS = 0$ and $dV = 0$

$$\Rightarrow dU = 0 - 0 + \mu dN$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Summary of results for internal energy and entropy --

$$U = U(S, V, N) \qquad dU = TdS - PdV + \mu dN$$

$$S = S(U, V, N) \qquad dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

Some first derivative relationships --

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}$$

Some second derivative relationships (thanks to Maxwell) --

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \qquad \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \qquad \left(\frac{\partial P}{\partial N}\right)_{S,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{S,N}$$

What can we do to rationalize these interdependencies? General notions of mathematical transformations for continuous functions of several variables and Legendre transforms --

Consider: $z(x,y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

$$\text{Let} \quad u \equiv \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad v \equiv \left(\frac{\partial z}{\partial y}\right)_x \qquad dz = u\,dx + v\,dy$$

Define new function

$$w(u,y) \quad \Rightarrow \quad dw = \left(\frac{\partial w}{\partial u}\right)_y du + \left(\frac{\partial w}{\partial y}\right)_u dy$$

For $\quad w = z - ux, \qquad dw = dz - u\,dx - x\,du = \cancel{u\,dx} + v\,dy - \cancel{u\,dx} - x\,du$

$dw = -x\,du + v\,dy$

$$\Rightarrow \left(\frac{\partial w}{\partial u}\right)_y = -x \qquad \left(\frac{\partial w}{\partial y}\right)_u = \left(\frac{\partial z}{\partial y}\right)_x = v$$

Desired thermodynamic functions --

Internal energy $U = U(S,V,N)$ $dU = TdS - PdV + \mu dN$

Entropy $S = S(U,V,N)$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

Enthalpy $H = H(S,P,N)$

Helmholtz free energy $F = F(T,V,N)$

Gibbs free energy $G = G(T,P,N)$

Using the Legendre transformation method:

$$H(S,P,N) = U + PV \qquad dH = TdS + VdP + \mu dN$$

$$F(T,V,N) = U - ST \qquad dF = -SdT - PdV + \mu dN$$

$$G(T,P,N) = F + PV \qquad dG = -SdT + VdP + \mu dN$$

Summary of thermodynamic functions

Internal energy	$U = U(S,V,N)$	$dU = TdS - PdV + \mu dN$
Entropy	$S = S(U,V,N)$	$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H = H(S,P,N)$	$dH = TdS + VdP + \mu dN$
Helmholtz free energy	$F = F(T,V,N)$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G = G(T,P,N)$	$dG = -SdT + VdP + \mu dN$

Various first derivative relationships

Some first derivative relationships --

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial H}{\partial S}\right)_{P,N} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V = \left(\frac{\partial H}{\partial P}\right)_{S,N} = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S} = \left(\frac{\partial H}{\partial N}\right)_{P,S} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

Which energy to use?

➔Choose the one that most easily describes the circumstances of the system

➔At constant T and P, the Gibbs free energy is often a good choice

Gibbs free energy $G = G(T, P, N) \qquad dG = -SdT + VdP + \mu dN$

Note also that $G = H - ST \qquad dG = dH - SdT - TdS$

Example -- consider the following reaction at fixed T (298 K) and P (1 bar)

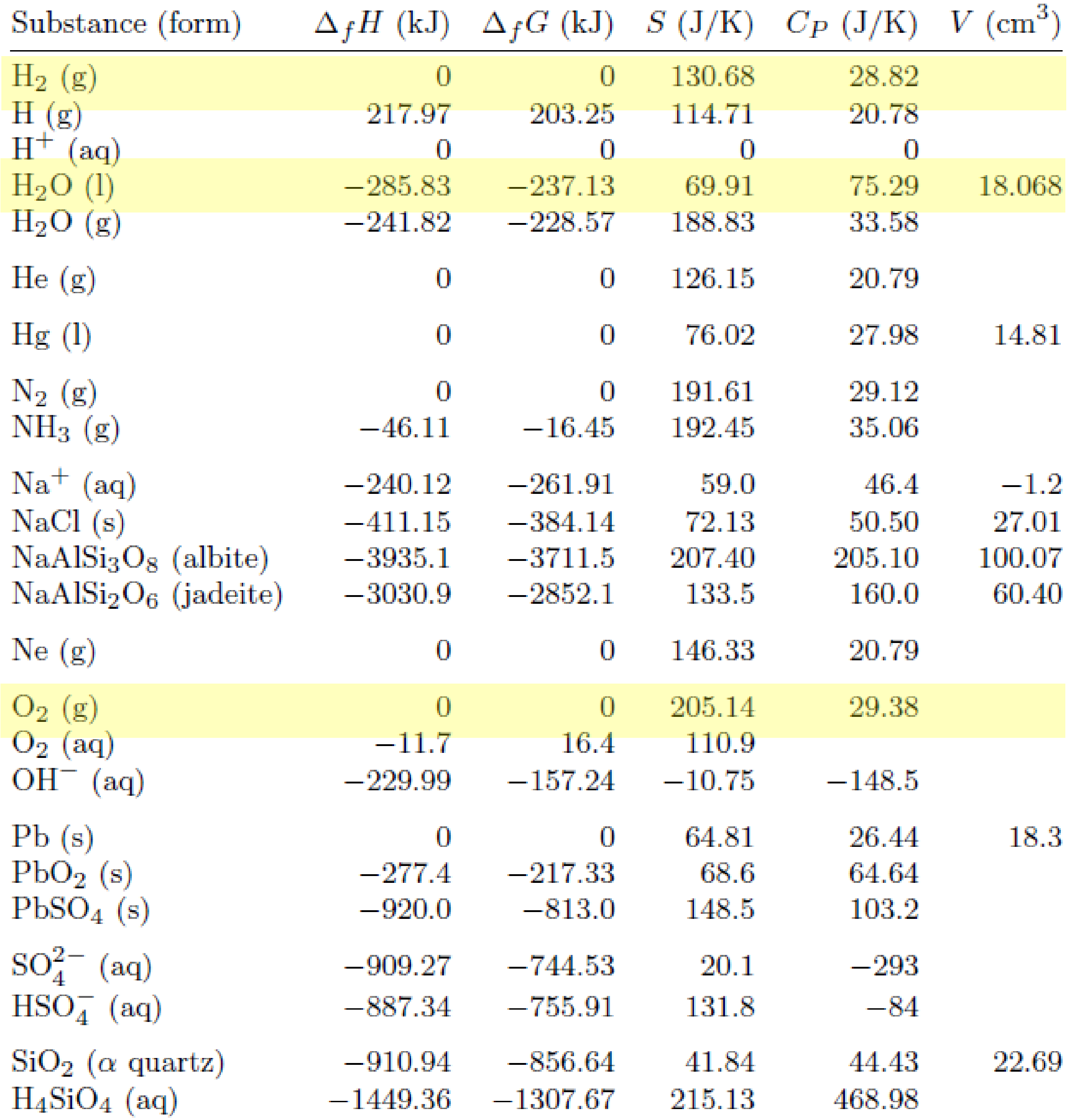
$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \frac{1}{2}\mathrm{O_2}$$

$$\Delta G = G_f - G_i = \mu_{\mathrm{H_2}} dN_{\mathrm{H_2}} + \mu_{\mathrm{O_2}} dN_{\mathrm{O_2}} - \mu_{\mathrm{H_2O}} dN_{\mathrm{H_2O}}$$

In this case, $dN_{\mathrm{H_2}} = dN_{\mathrm{H_2O}} = \frac{1}{2} dN_{\mathrm{O_2}} \equiv dN$

$$\Delta G = G_f - G_i = \left(\mu_{\mathrm{H_2}} + \frac{1}{2}\mu_{\mathrm{O_2}} - \mu_{\mathrm{H_2O}} \right) dN$$

Table of energies from your textbook for T=298 K and P=1 bar



Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
H_2 (g)	0	0	130.68	28.82	
H (g)	217.97	203.25	114.71	20.78	
H^+ (aq)	0	0	0	0	
H_2O (l)	−285.83	−237.13	69.91	75.29	18.068
H_2O (g)	−241.82	−228.57	188.83	33.58	
He (g)	0	0	126.15	20.79	
Hg (l)	0	0	76.02	27.98	14.81
N_2 (g)	0	0	191.61	29.12	
NH_3 (g)	−46.11	−16.45	192.45	35.06	
Na^+ (aq)	−240.12	−261.91	59.0	46.4	−1.2
NaCl (s)	−411.15	−384.14	72.13	50.50	27.01
$NaAlSi_3O_8$ (albite)	−3935.1	−3711.5	207.40	205.10	100.07
$NaAlSi_2O_6$ (jadeite)	−3030.9	−2852.1	133.5	160.0	60.40
Ne (g)	0	0	146.33	20.79	
O_2 (g)	0	0	205.14	29.38	
O_2 (aq)	−11.7	16.4	110.9		
OH^- (aq)	−229.99	−157.24	−10.75	−148.5	
Pb (s)	0	0	64.81	26.44	18.3
PbO_2 (s)	−277.4	−217.33	68.6	64.64	
$PbSO_4$ (s)	−920.0	−813.0	148.5	103.2	
SO_4^{2-} (aq)	−909.27	−744.53	20.1	−293	
HSO_4^- (aq)	−887.34	−755.91	131.8	−84	
SiO_2 (α quartz)	−910.94	−856.64	41.84	44.43	22.69
H_4SiO_4 (aq)	−1449.36	−1307.67	215.13	468.98	

Example -- consider the following reaction at fixed T (298 K) and P (1 bar)

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \frac{1}{2}\mathrm{O_2}$$

$$\Delta G = G_f - G_i = \mu_{\mathrm{H_2}} dN_{\mathrm{H_2}} + \mu_{\mathrm{O_2}} dN_{\mathrm{O_2}} - \mu_{\mathrm{H_2O}} dN_{\mathrm{H_2O}}$$

In this case, $dN_{\mathrm{H_2}} = dN_{\mathrm{H_2O}} = \frac{1}{2} dN_{\mathrm{O_2}} \equiv dN$

$$\Delta G = G_f - G_i = \underbrace{\left(\mu_{\mathrm{H_2}} + \frac{1}{2}\mu_{\mathrm{O_2}} - \mu_{\mathrm{H_2O}} \right)}_{237.13\ \text{kJ/mole}} dN$$

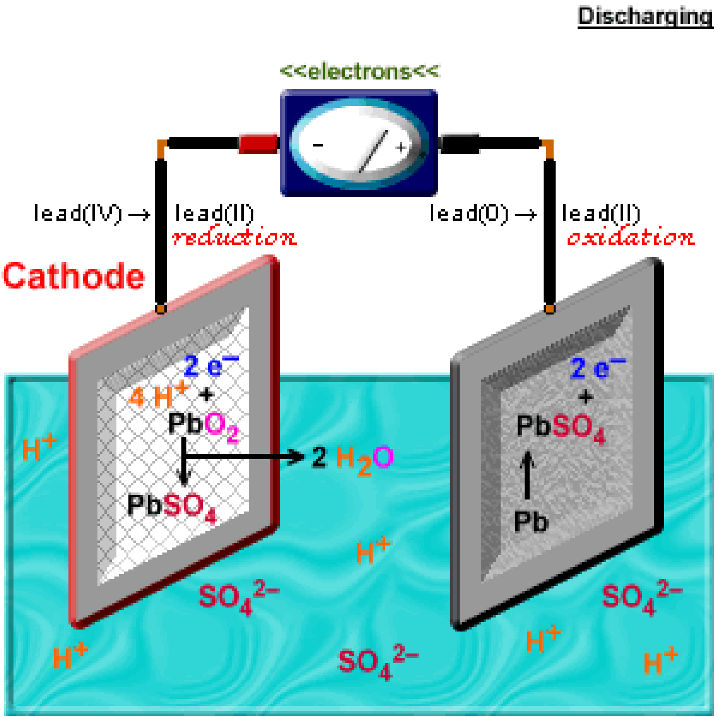
Electrochemical reactions

$$- \text{ electrode: } \mathrm{Pb} + \mathrm{HSO_4^-} \rightarrow \mathrm{PbSO_4} + \mathrm{H^+} + 2e^-$$

$$+ \text{ electrode: } \mathrm{PbO_2} + \mathrm{HSO_4^-} + 3\mathrm{H^+} + 2e^- \rightarrow \mathrm{PbSO_4} + 2\mathrm{H_2O}$$

$$\text{in solution: } \quad 2\mathrm{SO_4^{2-}} + 2\mathrm{H^+} \rightarrow 2\mathrm{HSO_4^-}$$

$$\text{net: } \quad \mathrm{Pb} + \mathrm{PbO_2} + 4\mathrm{H^+} + 2\mathrm{SO_4^{2-}} \rightarrow 2\mathrm{PbSO_4} + 2\mathrm{H_2O}$$



For each mole: $\Delta G = -394 kJ/mol = -2eN_{avo}\mathcal{V}$

$e = 1.60 \times 10^{-19} C \qquad N_{avo} = 6.02 \times 10^{23}$

$$\mathcal{V} = \frac{394000}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{23}} = 2 \text{ Volts}$$