Georgia Tech College of Engineering
School of Aerospace Engineering

Mixed Phase Equilibrium

- In a chemical equilibrium problem, what do we do if one (or more) of the species is a solid or liquid (condensed phase) - certainly can't assume TPG
  - e.g., $C(s) + O_2\,(g) \leftrightarrow CO_2\,(g)$ oxidation of solid carbon (e.g., graphite)
- Can still write Law of Mass Action (*equilibrium*) as $\Sigma \nu_i \mu_i = 0$
- For our example problem $\mu_{CO_2(g)} - \mu_{O_2(g)} - \mu_{C(s)} = 0$
  - and assuming gases (O_2, CO_2) are TPG $\mu_i = \mu_i^o + \bar{R}T \ln p_i$
  - combining $\mu^o_{CO_2} - \mu^o_{O_2} - \mu_C = -\bar{R}T(\ln p_{CO_2} - \ln p_{O_2})$
    or $\ln (p_{CO_2}/p_{O_2}) = -(\mu^o_{CO_2} - \mu^o_{O_2} - \mu_C) / \bar{R}T$

Georgia Tech College of Engineering
School of Aerospace Engineering

Mixed Phase Equilibrium

$$\ln (p_{CO_2}/p_{O_2}) = -(\mu^o_{CO_2} - \mu^o_{O_2} - \mu_{C(s)}) / \bar{R}T$$

function of T — *0, JANNAF element* — *function of T,p*

T (K)	$\Delta\hat{g}^o_{f,CO_2}$ (kJ/mol)
300	-394.4
500	-394.9
1000	-395.9
2000	-396.3

- Examine p dependence of μ_C (pure phase)

$$\left.\frac{\partial \mu}{\partial p}\right|_T = \hat{v} \Rightarrow \left.\frac{\partial \mu_{C(s)}}{\partial p}\right|_T = \hat{v}_{C(s)}$$

- Integrate at constant T from p^o to p

assume specific volume ~constant with p change (closer to incompressible)

$$\int_{p^o}^{p} d\mu_{C(s)} = \int_{p^o}^{p} \hat{v}_{C(s)}\, dp'$$

$$\mu_{C(s)} - \mu^o_{C(s)} \cong \hat{v}_C(p - p^o)$$

e.g., 1 bar

~5.3 cm^3/mol for graphite (3.4 cm^3/mol for diamond)

- Consider high pressure ($p - 1 \cong p$)
  - so $\mu_{C(s)} - \mu^o_{C(s)} \sim 0.5$ J/mol/bar $<< \mu^o_{CO_2} - \mu^o_{O_2}$

bar = 10^5 N/m^2 = 10^{-1} J/cm^3

Georgia Tech College of Engineering
School of Aerospace Engineering

Condensed Phase: p Dependence

- Like C(s), most condensed phases (solid/liquids) have small specific volumes (~10^{-1} – 10^{2} cm^3/mol)
  - compared to gases (10^{3} – 10^{5} cm^3/mol)
- Therefore $\mu(p,T) - \mu^o(T) \cong \hat{v}_C(p - p^o) \sim 0$
- So weak pressure dependence of μ for condensed species,
  - i.e., can assume $\mu(p,T) \cong \mu^o(T)$

Georgia Tech College of Engineering
School of Aerospace Engineering

Partial Equilibrium Constant

- So for our example

$$\ln(p_{CO_2}/p_{O_2}) = -(\mu^o_{CO_2} - \mu^o_{O_2} - \mu_C)/\bar{R}T$$

$$\frac{p_{CO2}}{p_{O2}} = e^{\frac{-(\mu^o_{CO_2} - \mu^o_{O_2} - \mu_C)}{\bar{R}T}} \cong e^{\frac{-(\mu^o_{CO_2} - \mu^o_{O_2} - \mu^o_C)}{\bar{R}T}}$$

- In general, can define a **Partial Equilibrium Constant**

$$K'_p(T) \equiv \prod p_i^{\nu_i} = e^{-\Delta G^o/\bar{R}T}$$

$\Delta G^o = \Sigma \nu_i \mu^o_i$

for gas phase species

  - assumed $\mu^o_i = \mu_i$; so need pure condensed phase, no solid mixtures or liquid mixtures
  - independent of amount of condensed phase present; but assumes enough of it present to reach equil. gas composition

Graphite Oxidation Example

from https://janaf.nist.gov/tables/C-095.html

Carbon Dioxide (CO_2) $C_1O_2(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p^o = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	C_p^o	S^o	$-[G^o-H^o(T_r)]/T$	$H-H^o(T_r)$	$\Delta_f H^o$	$\Delta_f G^o$	$\log K_{p,f}$
0	0.	0.	INFINITE	-9.364	-393.151	-393.151	INFINITE
100	29.208	179.009	243.568	-6.456	-393.208	-393.683	205.639
200	32.359	199.975	217.046	-3.414	-393.404	-394.085	102.924
298.15	37.129	213.795	213.795	0.	-393.522	-394.389	69.095
300	37.221	214.025	213.795	0.069	-393.523	-394.394	68.670
400	41.325	225.314	215.307	4.003	-393.583	-394.675	51.539
500	44.627	234.901	218.290	8.305	-393.666	-394.939	41.259
600	47.321	243.283	221.772	12.907	-393.803	-395.182	34.404
700	49.564	250.750	225.388	17.754	-393.983	-395.398	29.505
800	51.434	257.494	228.986	22.806	-394.188	-395.586	25.829
900	52.999	263.645	232.500	28.030	-394.405	-395.748	22.969
1000	54.308	269.299	235.901	33.397	-394.623	-395.886	20.679
1100	55.409	274.528	239.178	38.884	-394.838	-396.001	18.805
1200	56.342	279.390	242.329	44.473	-395.050	-396.098	17.242
1300	57.137	283.932	245.356	50.148	-395.257	-396.177	15.919
1400	57.802	288.191	248.265	55.896	-395.462	-396.240	14.784
1500	58.379	292.199	251.062	61.705	-395.668	-396.288	13.800
1600	58.886	295.983	253.753	67.569	-395.876	-396.323	12.939
1700	59.317	299.566	256.343	73.480	-396.090	-396.344	12.178
1800	59.701	302.968	258.840	79.431	-396.311	-396.353	11.502
1900	60.049	306.205	261.248	85.419	-396.542	-396.349	10.896
2000	60.350	309.293	263.574	91.439	-396.784	-396.333	10.351

- Our C(s)+$O_2 \leftrightarrow CO_2$ example is formation reaction for CO_2
- So $K_p' = K_{p,f\,CO_2}$
  - $>10^{10}$ for T up to at least 2000K
  - so $p_{CO_2} >> p_{O_2}$ if both in equilibrium with C(s)
- As $T\uparrow$, $\log K_p \downarrow$
  - agrees with van't Hoff relation
    $d(\ln K_p)/dT = \Delta\hat{H}/\bar{R}T^2$
    <0

Liquid-Vapor Mixture Example

- Consider phase equilibrium between liquid and gas phases of water – in equilibrium
  $H_2O(g) \leftrightarrow H_2O\,(l)$
  so if mixture includes both phases, will need to add this expression to list of "reactions"
- Equilibrium still given by $\Sigma \nu_i \mu_i = 0$
  - again assuming gas is TPG and $\mu_{H_2O(l)} \cong \mu^o_{H_2O(l)}$

$$-\bar{R}T \ln p_{H_2O} = \left(-\mu^o_{H_2O(g)} + \mu^o_{H_2O(l)}\right)$$ **Gibbs Free Energy of Phase Change**

- $p_i(T)$ = vapor pressure, function of T only
- $\mu^o_{(g)} \neq \mu^o_{(l)}$ since at equilibrium showed $\mu_{(g)} = \mu_{(l)}$